METALLOGRAPHY

PRINCIPLES

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BY

SAMUEL L. HOYT

PART I.—PRINCIPLES

II.—THE METALS AND COMMON ALLOYS

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IN PREPARATION

METALLOGRAPHY

PART I

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FIRST EDITION

THIS BOOK
IS
LOVINGLY DEDICATED
TO J. W. H.

PREFACE

The present book is the outgrowth of a lecture course which I gave at the University of Minnesota to students specializing in metallography. It deals with the general principles of metallography and with some of the more important methods which are used to carry out general investigations in the metallographic laboratory. It is my intention to deal, in subsequent volumes, with the metallography of the more important metals and alloys, including steel, cast iron and the special steels, and the applications of metallography to the metallurgical and engineering industries. On account of the nature of the subject, certain of the important principles have been withheld for discussion simultaneously with the phase of the work with which they were most closely associated. For this reason the newer ideas on plastic deformation and grain growth will be considered in connection with the application of metallography to technical practice.

The material presented naturally reflects my personal experience but it has been collected from every source which was available to me and presented in a manner as free from prejudice as possible. In cases where the subject matter is controversial both sides have been discussed, and, as far as possible, from the point of view of the principal proponents of the theories advanced.

The very scope of the work makes it well nigh impossible to give adequate acknowledgement to all persons whose thoughts and work are represented here but the desire has been always to give due credit for the material presented; but I, like others in this field, am deeply indebted to that great body of workers, both past and present, who have applied themselves to the study of the metals and their alloys and whose work has placed the science of metallography in the position it now occupies. I am also indebted to those who have kindly consented to the use of certain illustrations in the text. My particular thanks are due to Dean Appleby for permitting the use of illustrations in the collection at the School of Mines, and also for the friendly spirit he has shown towards this work during the time I served under him. It is also my pleasant duty to express my warmest

appreciation and thanks to Miss Carrie Green, Assistant in the Department of Metallography, for the intelligent and faithful assistance she has rendered throughout the compilation of these notes.

My special indebtedness and thanks are due to Mrs. Hoyt, who has been ready at all times to read the copy and has given much valuable assistance in the preparation of the manuscript.

S. L. H.

Nela Park, Cleveland, Ohio,
January, 1920.

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PART I

PRINCIPLES OF METALLOGRAPHY

CHAPTER I

CONSTITUTION DIAGRAMS

The Phase Rule.[1]—Leaving out of consideration the action of
gravity, magnetic, capillary, and various other forces, Gibbs re-
garded a system as possessing only three independently variable
factors—temperature, pressure, and volume or its equivalent, the
concentrations of the components of the system. This means
that it is by varying these three factors that changes in state or
constitution can be brought about; thus, by lowering the tem-
perature, we can convert substances from the liquid to the solid
state; or, by raising the temperature, we can convert them into
the vapor or gaseous state. In the same way, we can gasify or
liquify substances by alternately lowering and raising the pres-
sure on the system; or we can even convert solids into liquids by
subjecting them to great pressure, an example of which is to be
found in the effect of great pressure on ice at temperatures below
0°C. Changes in state produced by varying the concentration
of the system are less common, although the liquification of ice
by means of common salt or of solid iron by means of carbon, are
examples which are quite familiar. This is the fundamental con-
ception of the phase rule; and simple as it is, it has enabled phys-
ical chemists to correlate apparently unrelated phenomena and
to study them from a common point of view. Under this con-
ception the solidification of water or an aqueous solution, the
freezing of a rock magma or a molten alloy, or the precipitation

[1] For a more complete account of the Phase Rule and its applications, see
ROOZEBOOM, "Die heterogenen Gleichgewichte;" TAMMANN, "Krystalli-
zieren und Schmelzen;" and FINDLAY, "The Phase Rule," 1911, which
have been freely consulted in the preparation of this text.

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of a salt from solution by evaporation and other kindred phenomena all fall in the same category and may be treated by means of this rule. So upon this assumption, Gibbs developed a mathematical expression of the condition of equilibrium of a system expressed as a relationship between the number of what are called the "phases" and the "components" of a system.

The points involved here, while simple in themselves, are not readily grasped and so will be brought out one by one and discussed as simply as possible. Their application and use will be discussed as the need arises during the discussion of constitution diagrams.

Phases.—In the phraseology of the phase rule, those homogeneous, physically distinct, and mechanically separable portions of a system are called "phases." Ice, water, and water vapor are three phases of the substance, water. Calcium carbonate, calcium oxide and carbon dioxide are phases occurring in the dissociation of $CaCO_3$—two solid and one gaseous. Solid lead and molten lead are phases of the element lead, while solid lead and molten lead with tin dissolved are, again, two phases. A solution, whether it be solid or liquid, and irrespective of the amounts of the dissolved substances, is always regarded as but one phase.

An important point here is that the amounts of the phases present in a system have no effect on the equilibrium. Ice and water coexisting at 0°C. and atmospheric pressure are in equilibrium and the addition or subtraction of either produces no change in that equilibrium. The amount of the solid lead can be increased or decreased without affecting the composition of the molten lead-tin alloy, with which the solid lead is in equilibrium. In the same way, the amount of the molten lead-tin alloy can be varied at will without affecting the solid lead.[1]

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[1] There must be no confusion here between this statement and the law of mass action. Let us take, for example, dissociation of solid NH_4Cl into NH_3 and HCl, two gases. The two gases which come off are perfectly miscible in each other and form one homogeneous phase. According to the statement in the text, the addition or subtraction of either phase, as a whole, has no effect on the system, it being understood that the pressure remains the same. According to the law of mass action, the addition or subtraction of either NH_3 or HCl, constituents of the gaseous phase, would affect the equilibrium. In the same way the addition of molten tin to the molten lead-tin alloy which we assume is in equilibrium with solid lead, would liquify all or a part of the solid lead, depending on the shift in the total composition.

In metallography we find that most alloy systems have only one liquid phase but that some have two, and some even more, while the number of solid phases may be only one, but frequently is two or more. With the phase rule we can determine the greatest number of these phases which, for given conditions of temperature and chemical composition, can coexist in stable equilibrium.

Components.—By the number of the components of a system, is understood the smallest number of its constituents the concentrations of which can undergo independent variation. In metallography the systems (either metals or alloys) are composed of metals, or of metals and certain alloy-forming elements, so that the number of components is simply the number of elements present.

The Degrees of Freedom or Variability of a System.—The number of degrees of freedom or the variability of a system is taken as the number of the variable factors, temperature, pressure, and concentration of the components (in the phases), which must be arbitrarily fixed in order that the condition of the system may be perfectly defined (Findlay).

Water is an example of a one-component system which has two degrees of freedom. It is necessary to know both the temperature and pressure before the condition of the system is known, for both the temperature and pressure can have any one of a series of values. Water and ice in contact furnish an example of a system which possesses only one degree of freedom. If, for example, the temperature is known to be 0°C., the pressure is at once known to be atmospheric, for at no other pressure can ice and water coexist at 0°C. Varying the amounts of the phases present has no effect on the variability, but, as we shall see directly, varying the components has a direct effect.

The Phase Rule.—The phase rule is a mathematical expression of the relation between the degrees of freedom and the number of components and phases which a system has under conditions of stable equilibrium. It is expressed as follows:

$$F = C - P + 2$$

where F equals the number of degrees of freedom, C the number of components and P the number of phases.

Applying this rule to the above systems of water and ice plus water, we see that in the first case $C = 1$ and $P = 1$ so

that $F = 1 - 1 + 2 = 2$; *i.e.*, the system has two degrees of freedom and is said to be "bivariant," while in the latter case $P = 2$ and $F = 1 - 2 + 2 = 1$, so that the system has one degree of freedom and is said to be "uni-" or "monovariant." Systems with three degrees of freedom are "tri-" or "multivariant;" systems with no degrees of freedom are "invariant" or "nonvariant."

In metallography, pressure as a variable may usually be neglected as it remains constant (atmospheric) throughout most of the operations and, furthermore, the volume changes are small so that the influence of pressure is negligible. If one of the variables is eliminated, a degree of freedom is automatically subtracted so that we may restate the phase rule for our purposes as—

$$F = C - P + 1$$

According to this statement of the phase rule, water is a monovariant system, as temperature alone can be varied, while ice and water in contact form a nonvariant system, because the temperature can have only one value, 0°C.

Limitations of the Phase Rule.—The application of the phase rule to metallographic problems is somewhat limited because it applies to conditions of stable equilibrium, which requires that each phase must be (1) physically and chemically homogeneous and (2) in stable equilibrium with the other phases. In other words, the system must satisfy the conditions of homogeneous and heterogeneous equilibrium before the phase rule can apply in the strictest sense. The limitations of the phase rule are due to the failure of the metallic alloys to meet one or both of these requirements. Certain of the more important points in this connection will be pointed out from time to time.

We come now to the study of the behavior of metals and alloys from the standpoint of the phase rule, which means a study of the phasial changes which are produced by varying the temperature and concentration, and of the conditions of equilibrium while the changes take place. It is true that conditions of stable equilibrium are assumed for the purposes of this discussion, and that seldom are these conditions realized in metallographic practice, but it is only by acquiring knowledge of the ultimate tendency of the systems during their transformations that the variations and exceptions to this tendency can be intelligently applied. While the validity of this statement is held to be self

evident, certain illustrations will be given from time to time to show the difference between theories or explanations which have as their foundation the laws of heterogeneous equilibria and certain modifications due to the intercession of other equally fundamental laws of nature, and other theories which relate merely to a series of experimental data without correlation to the laws just mentioned. This part of the work might be termed a study of the static equilibria which occur in pure metals and binary alloys, leaving for later consideration the actual behavior of the systems during change of temperature.

In the discussion here, we shall consider single-component systems, two-component systems, and three-component systems. The phasial changes of the former are limited to changes in state and changes of the solid metal from one form to another. In multi-component systems it is possible to vary the second variable, the concentration of the components in the phases, which means that the phases can vary in composition.

One-component Systems. *Water.*—For practical purposes we shall here use pressure as a variable. It is well known that the boiling point and the freezing point of water depend on both the temperature and the pressure. At atmospheric pressure water boils at 100°C. and freezes at 0°C., but if the pressure is increased, the boiling point is raised, while the freezing point is lowered.

It is both useful and convenient to represent these facts graphically which may be done by means of the so-called "constitution diagram" of water in Fig. 1. This diagram shows at a glance the condition of the substance water at different values of the temperature and pressure. As a matter of course, this diagram brings out the effect of pressure on the boiling and freezing points. The three fields marked solid, liquid and gas, give the pressures and temperatures at which ice, water and water vapor are the stable phases. The lines bounding the three fields give the temperatures and pressures at which the two adjacent phases can coexist, while the intersection of the three fields, *O*, called the "triple point," gives the temperature and pressure at which ice, water and water vapor can coexist. It will be noticed that there is one, and only one, point on the diagram at which all three phases can coexist, viz., +0.0076°C. and 4.6 mm. Hg.

Applying the phase rule in its general form to the latter system

we see that ice, water and water vapor (three phases and one component) constitute a nonvariant system, *i.e.*, as soon as it is known that all three phases are together in physical contact (stable equilibrium assumed) it is known that the temperature and pressure are at the triple point   It is also known that were either the temperature or the pressure to vary from the triple point, one or two of the phases would immediately disappear. Again, if it is known that ice and water coexist (two phases, one component), the system is monovariant and it is known at once that the temperature and pressure will be given by some point
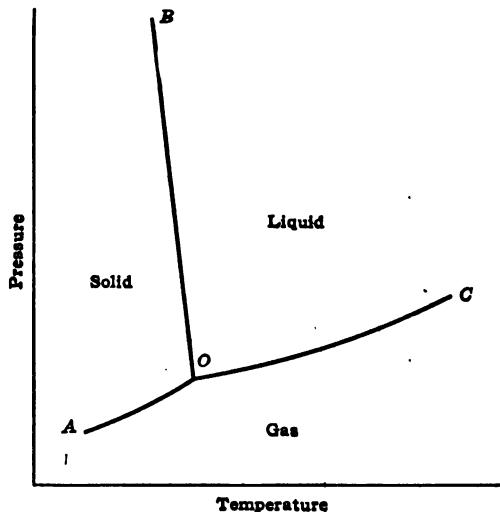
Fig. 1.—Constitution diagram of water.

on the line *OB*.   As soon as either the temperature or the pressure is known, the point is fixed.   In this case the variation of either the temperature or pressure might cause one of the phases to disappear but it is entirely possible to vary one of the variables without affecting the phases although the other variable would also have to change, and the change would be confined to the line *OB*.   The same applies to the systems water-water vapor and ice-water vapor.   If only one phase is present (one phase, one component) the system is bivariant and we must know both the temperature and pressure before we know the conditions under which the system exists.

Returning now to the conditions met in metallographic prac-

tice, in which case we are limited to atmospheric pressure, we see that the principal phasial change is from the solid to the liquid state or vice versa. This temperature is the so-called "melting point." By applying the phase rule, we may draw the important conclusions that melting or solidification takes place at constant temperature, *i.e.*, during the process the temperature remains constant, and that the melting point and solidification point coincide. These conclusions follow from the fact that the system becomes, for the time being, nonvariant which means that as long as and whenever the solid metal and molten metal coexist in stable equilibrium, the temperature must be the equilibrium temperature. Of course as soon as one of the phases disappears the heating, or cooling, can continue.

Polymorphism and Transformations in the Solid State. *Sulphur.* A similar study could be made of sulphur but it will suffice here to discuss the phenomenon of polymorphism[1] as exemplified by this substance. Polymorphic substances are those which occur in two or more distinct forms differing as to specific gravity, color and other physical properties. As used in metallographic parlance, polymorphism implies that each form, or "modification," is stable over a definite range of temperature (atmospheric pressure assumed) and that at some temperature, called the "transformation point," the two modifications can coexist in stable equilibrium. The modification which is stable above the transformation point is called the "high temperature modification" and the one stable below, the "low temperature modification." The term "transformation point" is used in place of the term "equilibrium temperature" because on passing this temperature the one modification may, and usually does, change or "transform" into the other.

Molten sulphur solidifies at 120°C. as long yellow crystals which belong to the monoclinic system. This yellow prismatic sulphur is stable from the melting point down to 96°C. when a red variety, belonging to the orthorhombic system, becomes stable. Consequently 96°C. is the "transformation point" above which the yellow variety is the stable form and below which the red variety is the stable form.

If we apply the phase rule to the system at 96°C. we find that $F = 1 - 2 + 1 = 0$. This tells us merely that when red sulphur and yellow sulphur coexist and that as long as the equilibrium is

[1] This phenomenon is also called "allotropy."

stable, the system is nonvariant and the temperature must be 96°C. From this we can then draw the important conclusion that if red sulphur and yellow sulphur are' known to coexist but at some temperature other than 96°C., one of the phases is not stable. Without the phase rule this fact would be obscured and our conception of the behavior of sulphur would be confused. As a matter of fact the transformation of yellow sulphur into red sulphur and vice versa is quite "sluggish" and actually we can have yellow sulphur at room temperature, or we can heat red sulphur up through 96°C. and melt it at 114°C. without changing it into yellow sulphur. The molten sulphur is metastable and, at some temperature below 120°C., solidifies as yellow sulphur which amounts to solidification on rising temperature. For a long time, this phenomenon was regarded as a mystery; but in the light of the phase rule and the well-known behavior of substances in over-stepping their transformation points, it is perfectly clear. The important point that the phase rule tells us, is that yellow sul-phur and red sulphur have an equilibrium temperature from which we can infer that yellow sulphur when below, and red sulphur, when above 96°C. tend to change their form. In a later chapter we shall study the laws governing the rate at which such trans-formations occur and some of the reasons for so-called "suppressed transformations."

Tin.—The metal tin offers another example of allotropy or polymorphism. The common form, white tin, is stable only at temperatures above 18°C.; below this temperature, a gray variety is stable. This discovery was first made in the winter of 1867–68, when it was noted that certain blocks of tin which had been stored in the customs house in Petrograd had crumbled into a gray powder and so had apparently become worthless, although the nature of this phenomenon was not known until later. It was found by E. Cohen that white tin changes into gray tin at temperatures around −50°C. and that the true equilibrium temperature is 18°C. The transformation, except at very low temperatures, occurs with considerable sluggishness so that the change from the white into the gray variety is seldom observed, even though the temperature is appreciably below 18°C. Cohen showed further that the rate at which white tin transforms into gray tin increases with drop in temperature, until a maximum is reached at about −50°C. The gray tin has a greater specific volume than the white tin so that it forms in small gray powdery

lumps. This peculiar disintegration of tin is now called "tin plague."

Monotropic Transformations.—The transformations just discussed are truly allotropic transformations; and by this, is meant that they proceed in one direction on cooling and in the reverse direction on heating, and that each modification has a range of stability. There are other transformations, however, which are known to proceed in but one direction, in which case, the transforming substance is metastable. These transformations are called "monotropic" and the direction of the transformation does not depend, as allotropic transformations do, on the temperature. A well-known example of a monotropic transformation is marcasite→pyrite. The breakdown of iron-carbide into iron and graphite is generally considered to be of this type. Allotropic transformations are said to be "reversible" and monotropic transformations, "irreversible." Examples will be cited as they are met with.

CONSTITUTION DIAGRAMS.

Two-component Systems: Degree of Solubility.—Let us take up now the "binary alloys," formed by adding one metal to another so that the composition varies from one pure metal to the other. The number of phases which we can have, depends upon the degree of solubility in both the liquid and the solid states and upon the formation of intermediary phases, which may be due to the formation of new molecular complexes. Also the variability of the composition of the phases for either the liquid or the solid state depends upon whether we have complete miscibility, partial miscibility, or complete insolubility. These three degrees of solubility can be illustrated respectively by the three systems—water-alcohol, water-ether, and water-oil.

Water-alcohol.—Water and alcohol are completely miscible, so that we always have but one phase in no matter what proportions we may mix the two components. This phase is called a solution of alcohol in water or of water in alcohol, according to the predominant component. This degree of solubility is the usual case with molten metals and is quite common even with solid metals.

Water-ether.—If ether is added to water or if water is added to ether, there is in either case only a limited amount of the solute

dissolved, so that we have two phases, one a solution of ether in water and the other a solution of water in ether.   If the amount of water or of ether added is greater than that which will completely dissolve, the excess will form a second liquid layer which will be neither pure water nor pure ether, but the other saturated solution.   In other words, if the total concentration lies intermediate between the compositions of the two saturated solutions of ether in water and water in ether, the liquid phases which form will be, in all cases, the two saturated solutions, irrespective of the actual amounts of the water and ether present.   With this degree of solubility either phase may have a variable, although limited range of, composition.

Water-oil.—If oil is added to water it at once separates out on the surface, as the solubility of oil in water (and of water in oil) is practically zero.   Theoretically two substances can not be in physical contact in stable equilibrium and not dissolve each other at least to some slight extent, but for our purposes here we shall speak of "insolubility" even in a poly-component system, but always in the sense that the solubility is too low to be detected by the ordinary means.   In this case the phases are the pure metals or intermediary phases and, of course, can not vary in composition.

The Effect of Temperature.—Figure 2 shows the constitution diagram of two substances A and B which are partly miscible at room temperature, as water and ether.   The ordinates of this diagram represent temperature and the abscissæ, concentration. The vertical at A represents 100 per cent. A and the vertical at B represents 100 per cent. B.   Dividing the horizontal distance between A and B into one hundred equal parts, a mixture of A and B is represented by a vertical line whose horizontal distance from the B vertical represents the percentage of A, and whose horizontal distance from the A vertical represents the percentage of B, in the mixture.   The percentage of B can be read directly off the scale at the bottom, and the percentage of A is 100 less the percentage of B.

The diagram shows that at the temperature θ_1, A is capable of dissolving amounts of B up to the percentage of B represented by the point 1; likewise that B dissolves A up to the amount of A represented by the point 2, and that either phase, existing by itself, can vary in composition, the A-rich phase from A up to point 1, and the B-rich phase from B up to point 2.   If the

total composition lies between the points 1 and 2, the system consists of a mixture of the two saturated phases, 1 and 2. As the total composition varies from 1 to 2, the relative amounts of these two phases vary from 100 per cent. of the A-rich liquid at 1 to 100 per cent. of the B-rich liquid at 2.

By applying the phase rule to the study of either phase, we see that even though the temperature is fixed, θ_1, it is possible to vary the composition because $F = 2 - 1 + 1 = 2$. Fixing the temperature at θ_1, does not fix the concentration of the phase. When the two phases coexist, the case is different; because now
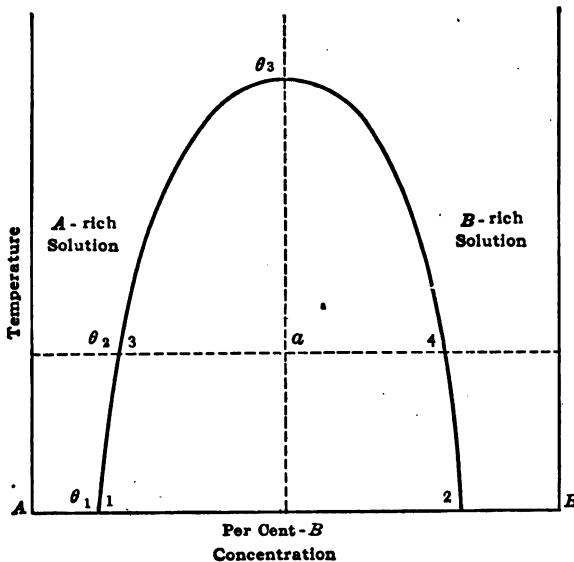
Fɪɢ. 2.—Solubility curves.

$F = 2 - 2 + 1 = 1$ so that once the temperature is fixed, at θ_1, the concentrations of the phases are fixed and they must correspond respectively to points 1 and 2.

Let us examine the system at another temperature, θ_2. The constitution diagram shows that at θ_2 ($>\theta_1$), A will dissolve B up to an amount represented by the point 3 which is, in general, although not necessarily, greater than the amount which can be dissolved at θ_1. Likewise, B can dissolve A up to an amount expressed by the point 4. If the total composition lies intermediate between 3 and 4, the system will consist of mixtures of the two saturated solutions, 3 and 4. At temperatures between

θ_1 and θ_2, compositions of the two saturated solutions are given by points on the lines 1–3 and 2–4, at the corresponding temperatures.

The two saturated solutions which are in equilibrium are known as "conjugate phases" and the two lines, 1–3 and 2–4, are known as "conjugate lines." The field bounded by the two conjugate lines is known as a "field of heterogeneous equilibrium." Figure 2 shows that as the temperature increases still further, the solubility increases, until, at θ_3, A and B become soluble in all proportions, like water and alcohol.

We come now to two fundamental rules which are advanced in the hope that they will prove of assistance in interpreting constitution diagrams. It is believed that these rules, along with the phase rule, if applied logically, will make clear the constitution of a system of any concentration, at any particular temperature, as well as any change in the equilibrium which takes place with change in temperature.

Rule I. In a Field of Heterogeneous Equilibrium, to Determine the Compositions of the Two Phases which are Stable at any Temperature.—Draw the temperature horizontal; its intersections with the two conjugate lines bounding the heterogeneous field, will give the points representing the compositions of the two phases which are in equilibrium at that temperature.

Rule II. To Determine the Relative Amounts of the Two Phases. Draw the concentration vertical (or "characteristic line") representing the total concentration; the relative amounts of the two phases may be ascertained from the "lever relationship" using the two intersection points as the points of application of the two loads, and the intersection of the total concentration vertical and temperature horizontal as the fulcrum point. The loads required to maintain a balance, expressed in per cent., as computed for the two lever arms, give directly the relative amounts of the two phases.

To apply these rules at θ_2, we can proceed as follows: First, select the conjugate lines. Then draw the temperature horizontal θ_2 and we get, as the intersections with the two conjugate lines, the points 3 and 4, which represent the compositions of the two phases. To determine their relative amounts in a system of total composition represented by the point a, we draw in the vertical a. The distance between 3 and 4 is divided into two parts, 3–a and a–4, which are the lever arms for the points 3 and 4.

From the well-known lever relationship, the amount of 3: the amount of 4::a–4:3–a.

These rules apply only to the study of fields of heterogeneous equilibrium and to changes in heterogeneous equilibrium and not to the study of homogeneous fields, because in the latter the composition of the phase is always the same as the total composition of the system.

One of the greatest difficulties encountered in the study of metallography lies in the interpretation of constitution diagrams and, as all of the known binary alloys are represented by means of their constitution diagrams, the necessity of interpreting them is self-evident. These diagrams are generally laid down by skilled metallographists who, of course, require no assistance of the present kind; but with the beginner it is quite different. He should have positive guidance until he has familiarized himself with constitution diagrams, and the utility of the phase rule and Rules I and II lies in the fact that they offer just such guidance. Applications of these three rules will be brought out in the following pages.

THE FOUR TYPES OF CONSTITUTION DIAGRAMS

Constitution diagrams show changes from the liquid to the solid state (freezing and melting points), transformations which occur entirely within the solid state, limits of solid solubility, intermediary phases and intermetallic reactions. Naturally, different binary alloys are represented by different kinds of diagrams, but a survey of a large number of diagrams which have been determined has made it possible to classify them into four types, which classification will be adhered to.

Type I.—*The two metals are soluble in each other in all proportions both in the liquid state and in the solid state.* This is the degree of solubility illustrated by alcohol and water, and in this case we can have but two phases—one liquid and the other solid, although the composition of each can and does vary from 100 per cent. of one metal to 100 per cent. of the other metal. The liquid phase is called the "melt" and the solid phase is called a "solid solution." The difference between a solid solution and a liquid solution is the same as the difference between a solid metal and a liquid metal. The liquid solution is isotropic while the solid solution is anisotropic or crystalline, but either is a

true solution in that the components are perfectly miscible.[1] Outside of the metals, examples of solid solutions are not very common. Among the minerals, we have as examples the plagioclase series and pyrrhotite, in which sulphur is dissolved in varying amounts in FeS.

The German equivalent of solid solution is "Mischkristall" which, unfortunately has been translated into English as "Mixed Crystals." The term "Mischkristall" implies miscibility and, in German, is a satisfactory term to use, but the English equivalent, by some misfortune, implies a mechanical mixture of the components. In the present text the term "solid solution" will be used throughout. Two metals which are soluble in each other in this manner are said to be "isomorphous" and the alloys are referred to as "isomorphous solid solutions."

Type I–a.—The melting point varies continuously from that of one pure metal to that of the other pure metal. The diagram depicting this type is shown in Fig. 3. θ_1 and θ_2 are the melting points of the pure metals A and B. The diagram shows that the addition of A to B has a double effect; the melting point is lowered, and alloys of A and B, instead of solidifying and melting at a constant temperature, as the pure metals do, solidify or melt over an interval of temperature.

The upper line is called the "liquidus" and it gives the temperature at which, on cooling, solidification begins and, on heating, fusion is completed. The lower line is called the "solidus" and gives the temperature at which, on cooling, solidification is completed and, on heating, fusion commences. The solidus and liquidus are two conjugate lines bounding the field of heterogeneous equilibrium marked "Solid plus Melt" which gives the temperatures and concentrations at which the system is made up of two phases—the solid and the melt.

That alloys of this type should solidify over a range of temperature can be inferred from the phase rule. In this case $F = 2 - 2 + 1 = 1$, or during solidification, the system has one degree of freedom. This means that the two phases may coexist in stable equilibrium over a range of temperature, and also

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[1] Glass is often cited as an example of a solid solution as the different ingredients are in a state of perfect solution; *i.e.*, they can not be mechanically separated nor distinguished. As an illustration of a solid solution, glass may be a very enlightening example, but, strictly speaking, it is not a solid but a super-cooled and highly viscous liquid.

that the compositions of the phases can vary at the same time. With only one degree of freedom, however, as soon as the temperature is fixed the compositions of the phases are also fixed and may be determined by application of Rule I. The assumption of a binary alloy, of this type, of a degree of freedom during solidification conforms to what seems to be a general principle, *e.g.*, that a system will assume the maximum number of degrees of freedom of which it is capable unless constrained from doing so by some other factor
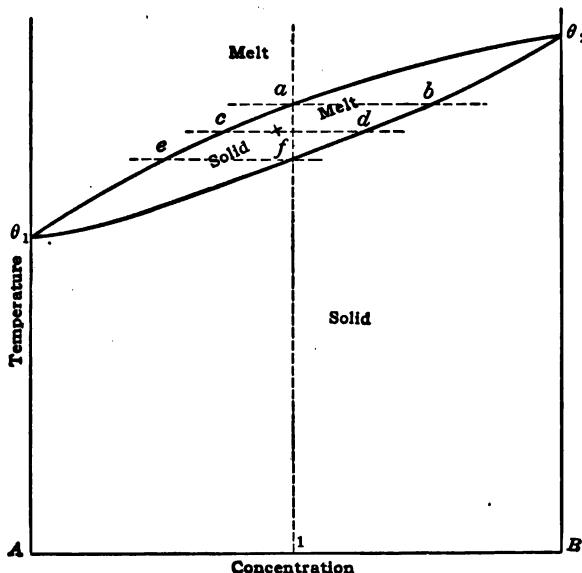
FIG. 3.—Type I-*a*. Complete solubility in liquid and solid states—the metals form isomorphous solid solutions.

By applying Rule I to this series we see that the solid which is first to form, on cooling, has a very different composition from the melt. Thus for alloy No. 1, by drawing a temperatur horizontal at *a*, the intersection of the concentration vertical with the liquidus, we get the intersection of this horizontal with the solidus at *b*, so that *b* gives the composition of the solid phase which is in equilibrium with the melt, and therefore which separates out of the melt. By applying the rule at lower temperatures, we see that the compositions of both plases change and are now given, for instance, by points *c* and *d*; or, in

other words, we see that, with drop in temperature, the composition of the melt varies along the liquidus, while that of the solid varies along the solidus. At the freezing point, we see that the composition of the solid corresponds to the total composition, while that of the melt is given by the point *e*.

The rate at which the solid phase forms on solidification and the liquid phase forms on fusion, can be followed by applying Rule II, which gives the relative amounts of the two phases present at any temperature. At the temperature *a–b*, Rule II shows that the amount of the solid phase is nil, *i.e.*, on solidification, the solid phase is just commencing to form; while at *c–d*, an appreciable amount of solid has formed, or about 50 per cent., as the two lever arms are approximately equal. As the temperature falls further, the solid phase continues to form at the expense of the liquid until, at *e–f*, the melt disappears. As soon as the alloy is completely solid, the system again has two degrees of freedom, and no further change takes place as the alloy cools to room temperature *A–B*.

For conditions during heating, Rule II will give the same relative amounts of the two phases as it did for conditions during cooling. This shows that alloy No. 1 just commences to melt at temperature *f* while of course the composition of the melt, which is present at this temperature in negligible quantities, has the composition *e*. As heating is continued, by applying Rule II to the successively higher temperatures, we would see that the amount of the liquid phase continually increases until at temperature *a* the alloy is completely molten.

Type I–b.—The freezing point curves pass through a minimum. This type of constitution diagram is shown in Fig. 4. According to this diagram, *A* and *B* are soluble in each other in all proportions in both the liquid and solid states, but the addition of either *A* to *B*, or of *B* to *A* lowers the range of solidification. At the minimum the liquidus and the solidus (must) intersect and the corresponding alloy melts or solidifies at constant temperature. This it must do, because one of the variables, being the concentration of the components of the phases, is eliminated and the system is, for the time being, nonvariant. It solidifies as if it were a pure metal, at constant temperature and without variation in the chemical composition of either phase.

An application of the two rules shows that the alloys of this system, intermediate between the minimum and the pure metals,

are not different from those of the system discussed under *I–a*, except that to the left of the minimum, the solid phase is always richer in *A* than the melt, while to the right of the minimum, the solid is always richer in *B* than the melt.[1]

Type II.—The two metals are soluble in all proportions in the liquid state, are incompletely soluble in the solid state, and the curves of primary solidification intersect at a minimum—the eutectic point. The solubility of the two metals in the solid state is represented either by the system ether-water, or oil-water.
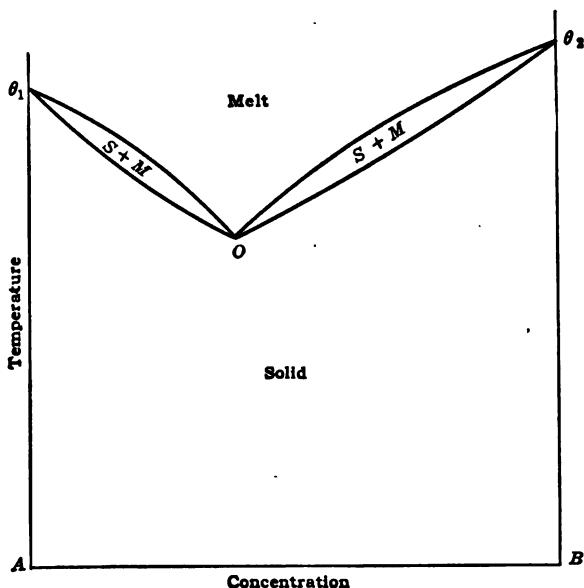
Fig. 4.—Type I-*b*. Complete liquid and solid miscibility—the liquidus passes through a minimum.

Type II–a.—The two metals are insoluble in the solid state. The constitution diagram representing this case is shown in Fig. 5. θ_1 and θ_2 represent the melting points of pure *A* and pure *B*. The addition of either *A* to *B* or *B* to *A* causes a depression of the melting point according to the well-known law of physical

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[1] This has suggested the rule that "the solid phase is always richer in that component whose melting point has been lowered." This rule is very often erroneously stated as "the solid is richer in that component which has the higher freezing point."

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chemistry.[1] This is represented in the above case by the lines $\theta_1 - o$ and $\theta_2 - o$, the slopes of which in terms of the atomic percentages of A or B per drop in temperature (degrees Centigrade) are known as the "atomic fall," according to Heycock and Neville.

By applying Rule I to the heterogeneous field marked "$A +$ Melt," whose conjugate lines are $\theta_1 - a$ and $\theta_1 - o$, we see that alloys of composition intermediate between pure A and o, as soon as their temperature falls to the liquidus (a point determined by the intersection of the total concentration vertical and $\theta_1 - o$) com-
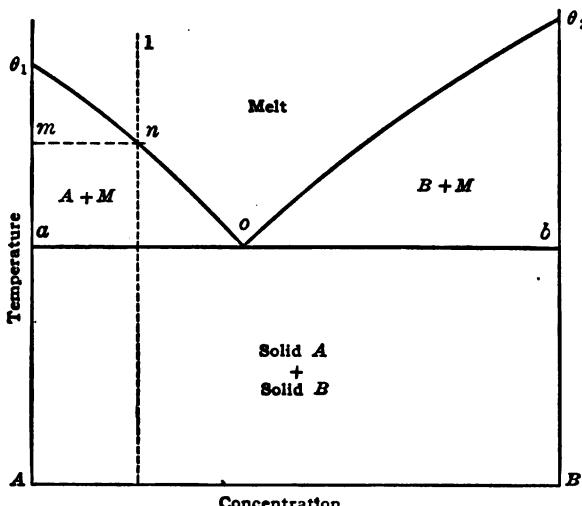
Fig. 5.—Type II-*a*.   Eutectiferous series—the metals are soluble in the liquid state and insoluble in the solid state.

mence to solidify by separating out pure A.   Here again we find that solidification takes place over an interval of temperature because $F = 2 - 2 + 1 = 1$, or the system is for the time being monovariant.   Inasmuch as it is always pure A which is in equilibrium with the melt, the solid phase does not vary in composition during solidification.   The liquid phase varies along the line $\theta_1 - o$ and the amount of solid A which forms in any particular alloy will be calculated from Rule II.   The same reasoning applies to the alloys between o and pure B as they solidify by separating out

[1] This law is known as Raoult's law and states that the addition of one molecule of B to A will lower its melting point by an amount which is independent of the nature of B.   This law holds for dilute solutions and in case the solid phase which separates out is one of the pure components.

pure B, the composition of the melt meanwhile varying along the line $\theta_2 - o$. It follows that the melt o, whose composition lies on both lines $\theta_1 - o$ and $\theta_2 - o$, at the temperature $a-o-b$, is in equilibrium with both A and B. Accordingly the melt of composition o solidifies by separating out both A and B simultaneously.

This enables us to trace the complete solidification of the alloys of A and B, which a typical case will suffice to make clear. Alloy ·(1) commences to solidify as soon as its temperature falls to $m-n$, when, according to Rule I, pure A commences to separate out. As the temperature continues to fall, according to Rule II, pure A continues to separate out while the melt concentrates in B, its composition following $\theta_1 - o$. When the temperature reaches $a-o-b$ the alloy is composed of about 50 per cent solid A and 50 per cent. melt of composition o. At this temperature the alloy completes its solidification when the melt o separates out both A and B simultaneously. The alloy of composition o has the lowest melting point of the entire series and, accordingly, is known as the "eutectic." All other alloys solidify in a manner analogous to (1) by separating out either A or B, according to which is in excess, until the composition of the melt reaches o, whereupon both A and B separate out together. The single exception to this is the eutectic which becomes saturated with A and B at the same moment, so that this alloy solidifies sharply at constant temperature at $a-o-b$.

An application of the phase rule to the fields A + Melt and B + Melt shows us that the system in either case has one degree of freedom. This means that at any one temperature there can be one and only one melt in equilibrium with A or one and only one melt in equilibrium with B, which is always given by the intersection of the temperature horizontal with the corresponding branch of the liquidus. The phase rule likewise tells us that during the freezing of the eutectic, there now being three phases in equilibrium, the system has no degrees of freedom. That is, there is one and only one temperature at which all three phases can coexist so that the temperature must remain constant during the solidification of the eutectic.[1]

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[1] It should at least be pointed out that it is theoretically incorrect to draw the eutectic horizontal intersecting the verticals at A and B. The principles of thermodynamics teach that a component will never separate out of a homogeneous solution of the two components absolutely pure. This point will be made clear under Type *II-b*.

During fusion the melt which is first formed has the composition o; in other words, the eutectic alloy is always the first to melt. If either A or B is in excess, it will be dissolved in the melt as the temperature increases, at a rate which is determined by Rule II. Here again the composition of the melt shifts along either $o-\theta_1$ or $o-\theta_2$ as the case may be. The alloy becomes completely molten as soon as the temperature along the concentration vertical enters the field marked Melt.
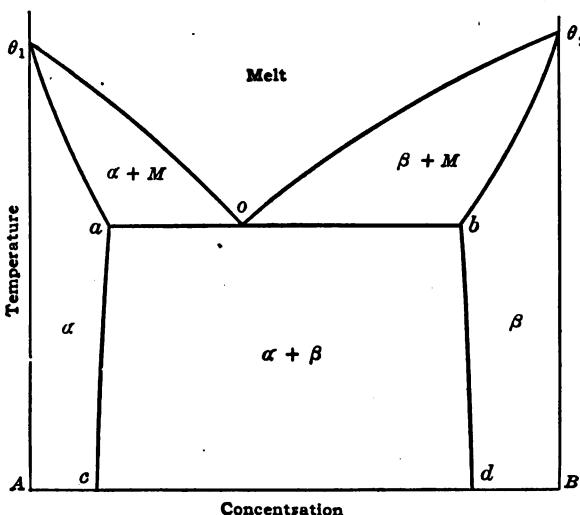
.Fɪɢ. 6.—Type II-*b*.   Eutectiferous series—the metals are partially soluble in the solid state.

Type II–b.—The metals are partly soluble in the solid state. The constitution diagram representing this case is shown in Fig. 6. The solid solution of B in A is designated as α and the solid solution of A in B as β. The compositions of α and the melt are given by the conjugate lines θ_1-a and θ_1-o, and of β and the melt, by the conjugate lines θ_2-b and θ_2-o, so that the process of solidification (or melting) of the simple solid solutions of this series can be traced as in *I–a* and *II–a*. The remaining alloys solidify as heterogeneous mixtures of the two saturated solid solutions α and β, in much the same manner as the alloys of Type *II–a* solidify as mixtures of A and B. The only differences are (1) that the solid phase forming in the melt varies in composition with drop in temperature, until its composition reaches the

saturation point, and (2) that the melt *o* (the eutectic) separates out the two saturated solid solutions, α and β, instead of the pure metals, *A* and *B*.

Type II–c.—One of the pure metals is the eutectic of the series. The constitution diagram representing this case is given in Fig. 7. θ_1 and θ_2 represent the melting points of the two pure metals *A* and *B*. Any alloy of *A* and *B* commences to solidify by separating out pure *A*, as soon as its temperature falls to a point on the line θ_1–θ_2. The process continues until the temperature
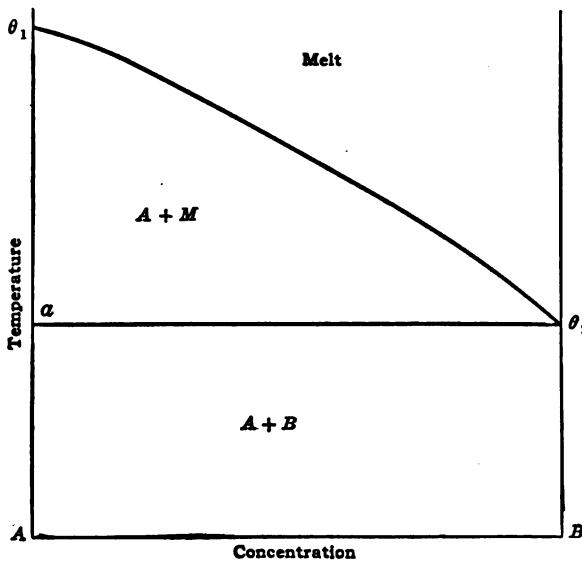
Fig. 7.—Type II-c. Eutectiferous series—pure *B* is the eutectic.

θ_2 is reached whereupon pure *B* solidifies, which is the last step in the solidification of the alloy.

Type II–d.—The metals form an intermetallic compound A_mB_n *which unites with A and B in two eutectiferous series.* The constitution diagram representing this case is shown in Fig. 8. The melting point of the compound, θ_3, is not governed by the melting points of the pure metals. As shown in Fig. 8, it can lie appreciably higher than either. The compound divides the series into two simple eutectiferous series, A–A_mB_n and A_mB_n–B, either of which corresponds to Type *II–b*. The two eutectics are mixtures of α and the compound (shown here, on theoretical grounds, as being slightly variable in composition)

and of β and the compound. The liquidus is divided into four branches corresponding to equilibria between α, β, and the compound and the melt.[1]

Type III.—The two metals are soluble in the liquid state, partially soluble in the solid state, and the curves of primary solidification intersect at a transition point corresponding to the "peritectic reaction." In systems of this type we have different phases in stable equilibrium with the melt above and below the transition or peritectic temperature. On this account the solid phase which separates out of the melt above the peritectic tem-
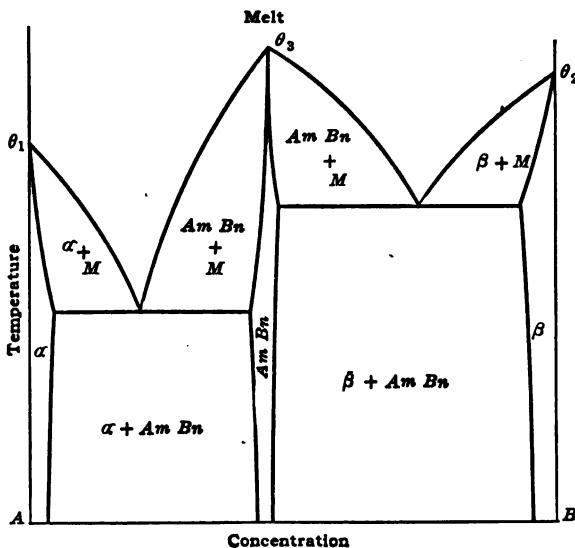
Fig. 8.—Type II-*d*. Eutectiferous series with an intermetallic compound.

perature reacts with the melt and produces the new solid phase. This reaction is called the "peritectic reaction."

Type III–a.—The product of the peritectic reaction is a solid solution. This type of constitution diagram is shown in Fig. 9. Alloys whose total compositions lie between pure A and a solidify according to Type *I–a* and therefore require no special discussion

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[1] An example of a series of this type is the Pb-Mg series. Magnesium melts at 635°C. and antimony at 630°C. but the compound Mg_3Sb_2 melts at 960°C. The primary constituents separating out of the melt are magnesium, the compound Mg_3Sb_2 and antimony, depending upon the total concentration. The two eutectics are Mg-Mg_3Sb_2 and Mg_3Sb_2-Sb.

here. Alloys between a and b commence solidification by the separation of the solid solution α, as a primary phase, and α continues to separate out until the temperature drops to $a-b$. The two phases in equilibrium at this temperature, as determined by Rule I, are α of composition a and melt of composition b. The peritectic reaction is given as

$$\alpha + \text{Melt} \rightleftarrows \beta$$

If α is in excess during the reaction the melt is completely used up so that we have left, as the two stable phases, α of composition a,
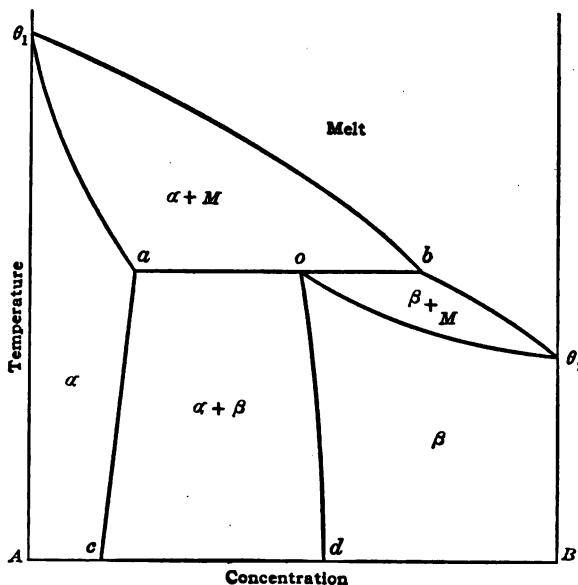
FIG. 9.—Type III-*a*. Peritectic series—point *o* is the peritectic point.

and β of composition o.[1] On further cooling the compositions of α and β follow the two conjugate lines $a-c$ and $o-d$.   If the melt is in excess, *i.e.*, if the composition lies between o and b, the α is used up during the reaction leaving β and the melt.   With further drop in temperature, solidification proceeds with continued separation of β until the temperature reaches the solidus.

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[1] Rule I shows that the melt disappears and that the β phase forms as the temperature falls through the peritectic temperature.   Rule II shows that the amount of the α phase decreases at the same time.   This confirms the above statement of the peritectic reaction.

Alloys lying to the right of b solidify, by the separation of the β solid solution, as the alloys in Type I–a, and do not require special consideration.

During the peritectic reaction there are three phases in equilibrium so that the temperature remains constant until either the α phase or the melt, or both, if the composition lies at the peritectic point, disappears.

Type III–b.—The product of the peritectic reaction is an intermetallic compound. The constitution diagram showing this case is given in Fig. 10. The chief difference between this case
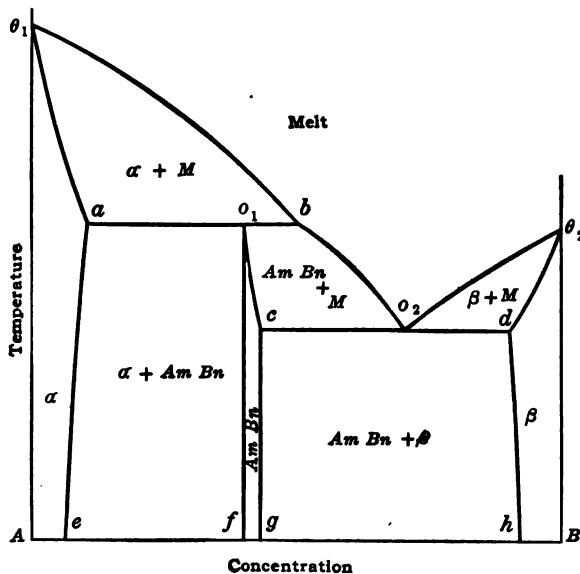
Fɪɢ. 10.—Type III-b. Peritectic series with an intermetallic compound.

and the preceding one is that the solid which forms during the peritectic reaction is an intermetallic compound. The solubility of A and B in the compound is shown to be very slight. The compound, as shown here, forms a eutectiferous series with B, but otherwise the series complies with Type III–a.

Type IV.—The two metals are incompletely soluble in both liquid and solid states. This case is not at all an uncommon one as there is quite a number of alloy systems which show two, and some even more, liquid phases. The cases discussed here should suffice to indicate the nature of the equilibria involved.

Type IV–a.—The metals are partially soluble in both liquid and solid states. This case is shown by Fig. 11. The liquidus in Fig. 11 is θ_1–b–c–θ_2 and the solidus is θ_1–a–d–θ_2. In the liquid state we have solubility corresponding to that of the ether-water system. Molten A and molten B are soluble in each other to the extent shown by the lines b–b' and c–c'. Systems whose total compositions lie between these two lines are composed of the two saturated melts 1 and 11 whose compositions for any temperature can be determined by applying Rule I.
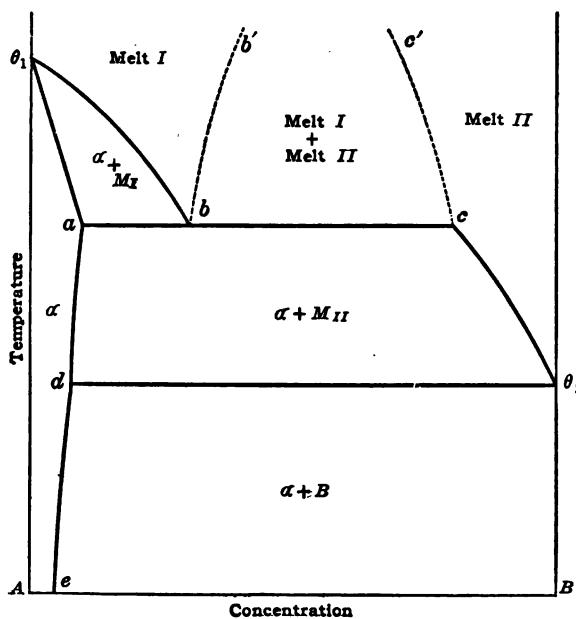
Fig. 11.—Type IV-*a*. Partial solubility in both the liquid and solid states.

In the field marked α + Melt I we have the α solid solution in equilibrium with the melt so that, on cooling, the α solid solution separates out of the melt. If the total composition lies to the right of a, the saturation point is exceeded and a certain amount of melt I, of composition b, will remain after the separation of the primary α. Turning now to the line b–b', we see that we have melt II in equilibrium with melt I, the compositions of which lie on the two conjugate lines b–b' and c–c'. According to the above, melt I of composition

b at the temperature *a–c*, is in equilibrium with both *α*, of composition *a*, and melt II according to the reaction

$$\text{Melt I} \rightleftarrows \alpha + \text{Melt II}$$
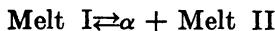
During the reaction the system is nonvariant so the temperature remains constant. As all compositions intermediate between *a* and *c* pass through this nonvariant system, a horizontal is drawn through *b*.

Returning to the alloys which lie between *a* and *b*, we see that their solidification proceeds according to the following: the *α* solid solution first separates until the temperature falls to *a–c*, whereupon the melt I splits up into *α* and melt II. The increase in the amount of *α*, during this procedure, can be determined from the relative amounts of *α* and melt I and of *α* and melt II. As soon as melt I disappears, the temperature can again fall and *α* continues to separate out; this time, however, it forms in melt II whose composition follows along the line *c–θ₂*. At the temperature θ_2, melt II is simply molten *B*, the solidification of which is the last step in the solidification of the alloy.

If the composition lies between *b* and *c*, the melt separates into two liquid layers before solidification sets in. As soon as the composition of melt I becomes *b* (at the temperature *a–c*) it breaks down into the *α* solid solution and additional melt II. From this temperature down, solidification proceeds as described above.

Alloys between *c* and *B* solidify in two steps by separating out *α* as soon as the temperature drops to the line *c–θ₂*, and by the solidification of molten *B*.

Type IV–b.—The metals are insoluble in both the liquid and the solid states. This case is represented by the constitution diagram shown in Fig. 12. θ_1 and θ_2 are, as before, the melting points of the pure metals *A* and *B*. As the alloys are insoluble in each other, their simultaneous presence in a system has no effect on the melting points so that *A* and *B* solidify at their normal freezing temperatures, θ_1 and θ_2.[1]

Experience shows that the average beginner has great difficulty in mastering the interpretation of constitution diagrams

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[1] Iron and silver offer an example of this type. So slight is the solubility of these two metals that silver can be melted in an iron crucible without contamination.

and yet, until this has been accomplished, he can hardly view the behavior of the metallic alloys in the true light. While no amount of reading can take the place of diligent study by the individual, the following are advanced as being among the important questions involved.

1. What phases are present in a system of a given total composition at a given temperature? This is shown by the constitution diagrams just as a map of the United States designates the various states of the union.

2. What compositions do the phases have? Apply Rule I.

3. How much of each phase is present? Apply Rule II.
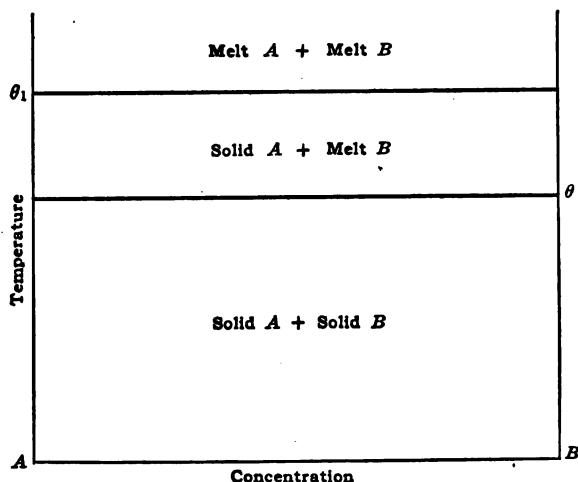
Fig. 12.—Type IV-*b*. The metals are insoluble in both the liquid and the solid states.

4. How does a system of a given composition vary with change in temperature? (*a*) In homogeneous fields, there can be no change in constitution with change of either temperature or concentration. The actual changes produced are due to other causes. (*b*) In heterogeneous fields there is likewise no change in constitution although the amounts and compositions of the phases can change and this can be followed by successive applications of Rules I and II. (*c*) Changes in constitution produced by crossing from one field to another can be seen at a glance from the diagram, as each field has marked on it the phase or phases which are stable under the governing conditions of temperature and concentration. These changes have just been discussed with the assistance of Rules I and II.

TRANSFORMATIONS IN THE SOLID STATE

The laws of heterogeneous equilibria are equally applicable to equilibria between solid phases as to equilibria between liquid phases or solid plus liquid.

First of all we shall divide polymorphic transformations into two groups, (1) those which depend on allotropic transformations of the components, and (2) those which are independent of allotropic transformations in the components.

As one of the simplest of the first group we have the type diagram shown in Fig. 13. θ_3 and θ_4 are the transformation points of A and B. The low temperature modifications are called α and the high temperature modifications β. The two β phases (βA and βB) and the two α phases (αA and αB) are
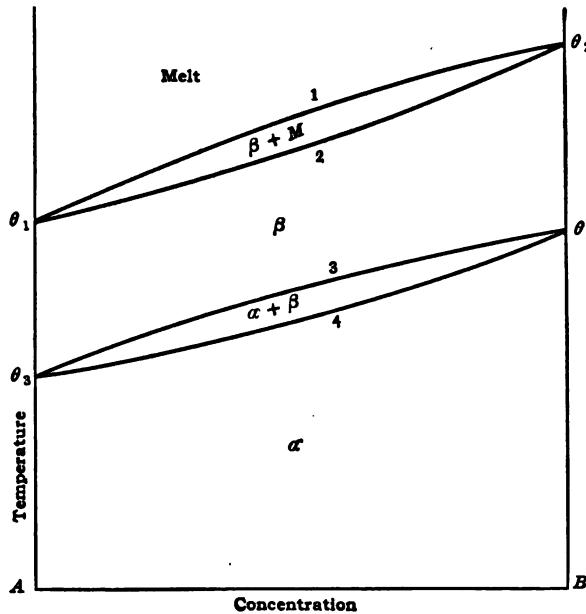
FIG. 13.—Polymorphic transformation—the high-and-low-temperature modifications are soluble in all proportions.

soluble in each other in all proportions, so that this case is identical with that described above as Type *I–a*. During the transformation of the β solid solution into the α solid solution, the system is univariant; from which we know that the transformation takes place over an interval of temperature while the compositions of the two phases, though variable throughout the transformation, are fixed at any particular temperature. This state of affairs is shown by the lines θ_3–3–θ_4 and θ_3–4–θ_4, conjugate lines bounding the heterogeneous field $\alpha + \beta$. The upper line is known as the "major" and the lower line as the "minor."

It is well to note that these transformation curves may pass through maxima or minima, whose compositions may or may not correspond to simple molecular relationships between *A* and *B*.

Another case met with, where only one of the metals is polymorphic, is illustrated by Fig. 14. *B* is soluble in both αA and βA and the addition of *B* lowers the transformation range, as shown by the lines $\theta_3 - a$ and $\theta_3 - b$.

It frequently happens that the addition of *B* to *A* raises the transformation point and if the major and minor intersect the
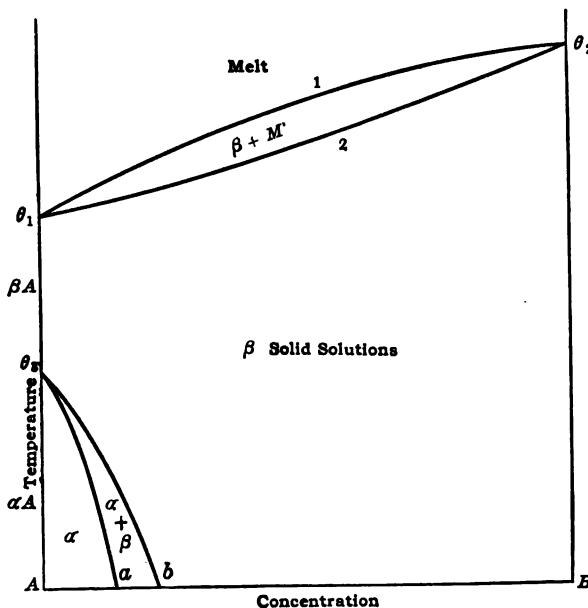
Fig. 14.—Polymorphic transformation.

fusion curves as a consequence, we get the case shown in Fig. 15. The β solid solution (solution of *B* in βA) separates out of the melt and transforms into α by passing through the univariant system $\alpha + \beta$, which has already been discussed.

At the point *a*, the β solid solution is in equilibrium with both the melt—the composition of which is given by the intersection of the temperature horizontal through *b* and the liquidus—and the α solid solution—the composition of which is given by the intersection of the temperature horizontal and the minor. On cooling, the equilibrium changes from $\beta +$ Melt to $\beta + \alpha$ which

is given by the peritectic horizontal through the peritectic point *o*.
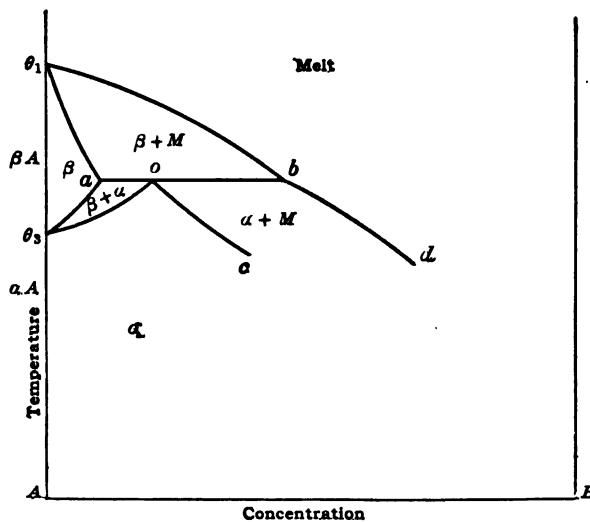
Fig. 15.—Polymorphic transformation—the major and minor intersect the solidus.

If the high temperature modifications are soluble and the low temperature modifications are insoluble, we have the case shown
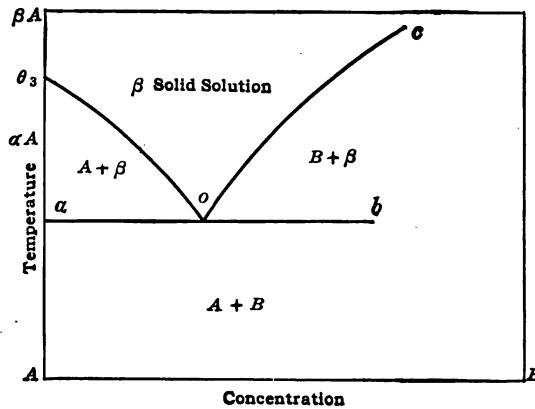
Fig. 16.—Eutectoid inversion. The β solid solution breaks down into $A + B$ at the eutectoid point 0.

in Fig. 16.   This case is analogous to Type *II–a* discussed above. The addition of *B* to *A* lowers the transformation point along the

line θ_s-o, so that along the line θ_s-o, αA is in equilibrium with the β solid solution. Along the line $o-c$, the B phase of Fig. 16 is in equilibrium with β. Therefore the point o corresponds to the eutectic point o of Fig. 5 and, accordingly, is called the "eutectoid" point. The transformation of the β solid solution into A and B is called the eutectoid "inversion" or "breakdown" and is represented by the reversible reaction

$$\beta \rightleftarrows A + B$$
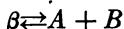
If the composition lies between a and o, the transformation commences with the primary separation of A, and the simultaneous shifting of the composition of β to the eutectoid point o. The
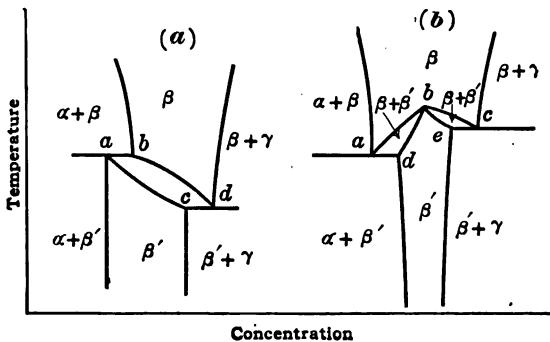
Fig. 17.—Polymorphic transformation of an intermediary solid solution.

transformation is completed by the breakdown of β into A and B. If the composition lies to the right of o, the transformation commences with the separation of B and the simultaneous shifting of the composition of β to o. As before, the eutectoid inversion completes the transformation.

The two leading types of the second group are polymorphic transformations and eutectoid inversions of intermediate solid solutions. The polymorphic transformation is shown in Fig. 17.

β, in transforming into β', passes through a univariant system, the variation of which is given by the lines $b-d$ and $a-c$ in 17a, and $a-b$ and $d-b$ and $b-c$ and $b-e$ in 17b. There have not been many cases of this kind which have been closely examined, so that the diagrams as given are based more on theory than on actual experiment. However it seems more than likely that the major and the minor will intersect, or nearly so, at the verticals bounding the β field.

A typical eutectoid of an intermediate solid solution is shown in Fig. 18. The solidification proceeds according to Type *III–a*. The β solid solution, which forms during the peritectic reaction and along the branch *b–d* of the liquidus, is stable only at temperatures above *e–o'–f* At the temperature *e–o'–f* it breaks down into $\alpha + \gamma$ according to the eutectoid inversion

$$\beta \rightleftarrows \alpha + \gamma$$
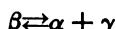
We have, as the general case, the separation of α along *o–o'* and of γ along *c–o'*, with the simultaneous shifting of the composition
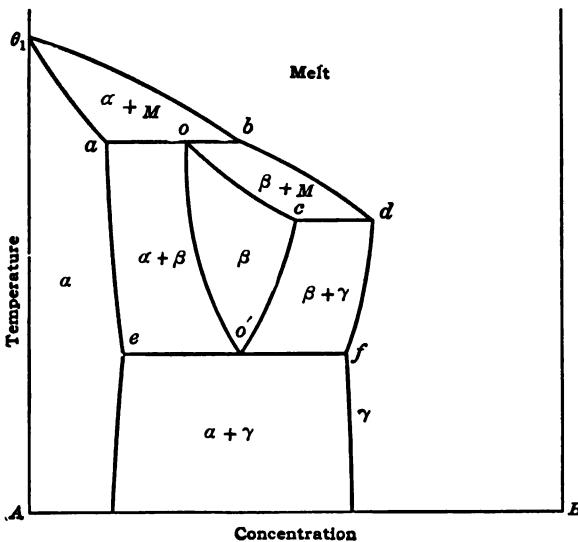
Fig. 18.—Eutectoid inversion of an intermediary solid solution.

of β, in both instances, to *o'*. The alloy of composition *o'* is the eutectoid and its behavior is the same as that discussed above.

The types of constitution diagrams described here do not give all the possible equilibria in binary systems, but they represent those types most commonly met with in the study of the metallic alloys. As the work done upon the alloys increases, new cases will doubtless be discovered, which will require modifications of the present types, or even new types, for their representation. There should be no difficulty in interpreting such new types, as well as certain isolated equilibria already recorded but not

included in the above discussion, as the laws of heterogeneous equilibria, and the three rules given, in particular, are perfectly general in their application.

Rules Governing the Construction of a Constitution Diagram. In order to construct a constitution diagram theoretically correct, it is necessary to recognize certain basic principles which govern the construction of all constitution diagrams. One of the most important of these is that a temperature horizontal should intersect, alternately, a field of heterogeneous equilibrium and a field of homogeneous equilibrium.

Again, two fields of heterogeneous equilibrium, one of which is directly above the other (ordinates = temperature), must have
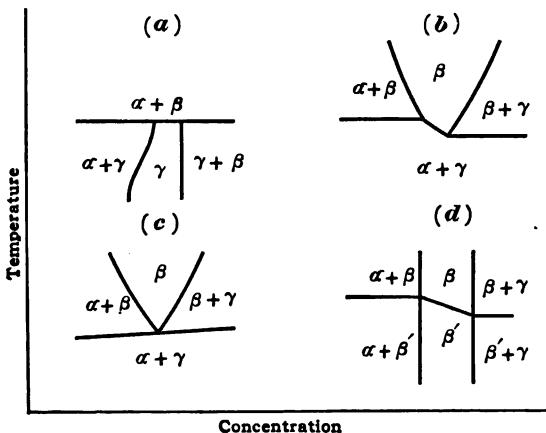
FIG. 19.—Incorrect constructions in constitution diagrams.

as their bounding line, a temperature horizontal corresponding to a nonvariant system. A field of homogeneous equilibrium, intersecting or touching the temperature horizontal, can do so only at a point. A quite common error is that shown in Fig. 19a in which the vertical lines bouding a homogeneous field intersect a temperature horizontal as shown on the left. According to this, one phase, either the α or the β, would be in equilibrium with an entire range of composition of another phase, the γ, which according to the phase rule is impossible. This error is eliminated by causing the two vertical lines to intersect at the temperature horizontal. A temperature horizontal corresponding to a nonvariant 3-phase equilibrium must be a continuous horizontal line, and not stepped or inclined as shown in b and c.

3

The polymorphic transformation of a solid solution should not be represented by a single straight line at an angle to the concentration axis, as shown at *d*, but by means of a major and minor, as shown in Fig. 17*a*. This also makes impossible the intersection of a vertical and a horizontal line in a constitution diagram. To make the true conditions evident the vertical line should be replaced by a field.

Ternary Equilibria.—The use of ternary constitution diagrams, and the study of ternary equilibria have not been as extensive in the past, as would seem to be justified by the use and importance of the ternary alloys. This may be explained as follows: The most important ternary alloys are customarily regarded as binary alloys to which a third metal has been added for the sake of producing some desired improvement. Thus we have the special steels, Admiralty metal (zinc bronze), and Naval brass (tin brass) which are essentially steels, bronzes, and brasses whose properties have been modified by certain additions. In addition to alloys of this type, we have other ternary alloys, like the bearing metals, which are more properly regarded as ternary alloys in which all three metals have a qualitative as well as a quantitative effect. These distinctions are not hard and fast but they explain, at least, why it is that some of the most important ternary are studied as binary alloys.

The laws governing the constitution and constitutional changes of ternary alloys are the same as those for binary alloys which have been considered in the foregoing. On applying these laws, however, we find that ternary equilibria are considerably more complex than binary equilibria. It has been the writer's experience that the principal reason for this is the difficulty in following the phasial compositions with change in temperature and composition. Some equilibria which are apparently simple remain practically insolvable of this account.

The complete ternary diagram, drawn with temperature and composition as coördinates, must be represented with a three dimensional space diagram. Compositions are given by points in an equilateral triangle, as is made clear in Fig. 20. *A*, *B*, and *C* are pure metals. Alloys of *A* with *B* and *C*, and of *B* with *C*, are represented here by the three sides of the triangle. The compositions of the binary alloys are given by points along the three lines, as is customary for binary alloys. The compositions of the ternary alloys are given by points within the triangle. This

method of representing ternary compositions is based on the theorem of geometry that the sum of the three perpendicular distances from any point within the triangle is always equal to the altitude of the triangle, which we may take as 100 per cent. In the figure, alloy (1) is represented by the point *o*. It contains *o–a* per cent. *A*, *o–b* per cent. *B* and *o–c* per cent. *C*. These diagrams are usually drawn on triangular coördinate paper so that the composition at any point can be read off direct. This coördinate paper makes it simple to plot alloy compositions, eutectic and other lines and phasial fields.
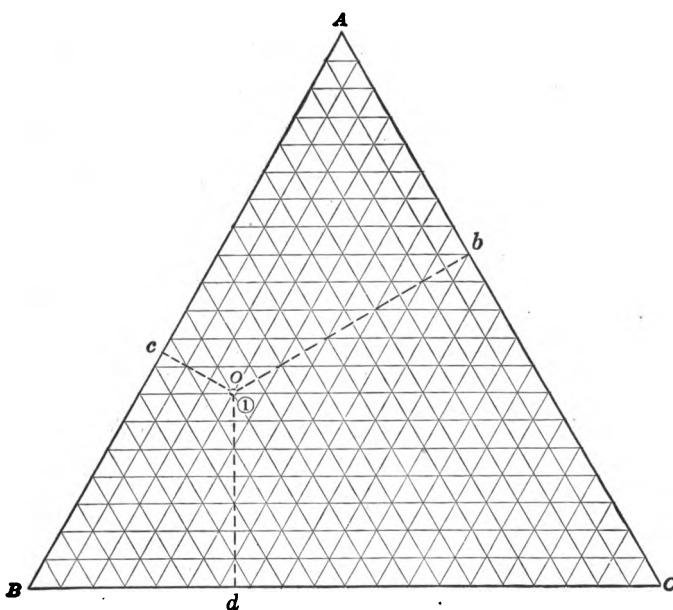
Fɪɢ. 20.—Method of representing ternary compositions.

Temperatures, and phasial changes produced by temperature changes, are represented by means of perpendiculars to the plane of the triangle *A–B–C*. This calls for a three dimensional model to represent the complete ternary diagram. It is obvious, however, that a single surface, such as the liquidus surface, can be shown by temperature contours and that the space model can be drawn in isometric or other projection. Another scheme, which is often resorted to, is to draw typical sections through the ternary diagram, although phasial changes can be represented in

this way only in case the section is that of a pseudo-binary system such as we sometimes have between inter-metallic compounds.

A simple case of a ternary system is shown in Fig. 21 which is the ternary diagram of lead, tin and bismuth, according to Charpy.[1] Lead, tin and bismuth are soluble in all proportions in the liquid state and, for the sake of simplicity are assumed to be insoluble in the solid state. Each binary pair has a eutectic, as shown, while the ternary alloys have a ternary eutectic of composition o and solidifying at 97°C. The contour lines
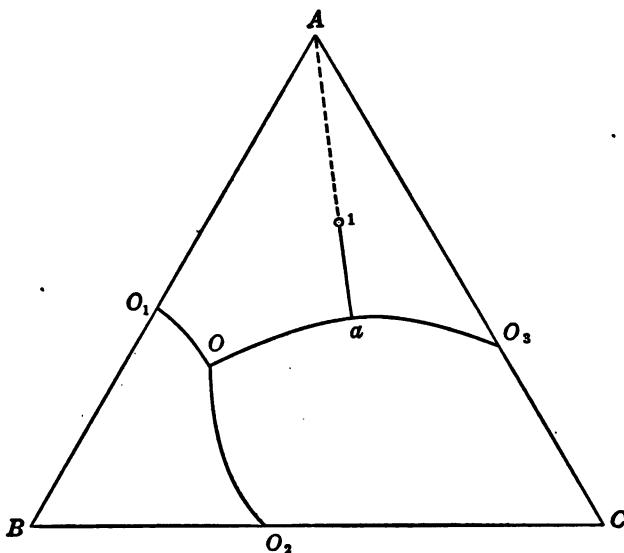
Fig. 21.—The lead-bismuth-tin ternary diagram.

give the three liquidus surfaces which intersect along the lines o_1–o, o_2–o and o_3–o. These three lines run along the bottoms of the "valleys" and give the compositions of the three binary eutectics in the corresponding ternary alloys.

The solidification of an alloy can be followed by means of alloy 1, which we may take as being typical of the ternary alloys. According to our hypothesis, pure lead separates out of this alloy as the first stage of solidification. We know it is lead which is first to form because the composition of the alloy falls on the lead

[1] CHARPY, Contrib. a l'etude d. Alliages., p. 203.

side of the line o_1–o–o_3. Now if pure lead separates out of the alloy, the composition of the melt must vary along a line which is the extension of the line drawn from A through 1, or along 1–a. During this time the temperature falls slowly. The melt finally has a composition a and, at the same time, becomes saturated with tin as well as lead. At this moment the binary eutectic of lead and tin commences to form. As the binary eutectic solidifies the composition of the melt varies along the line o_3–o until it finally reaches the composition o. The melt is now saturated with all three metals and the ternary eutectic of the three metals solidifies.
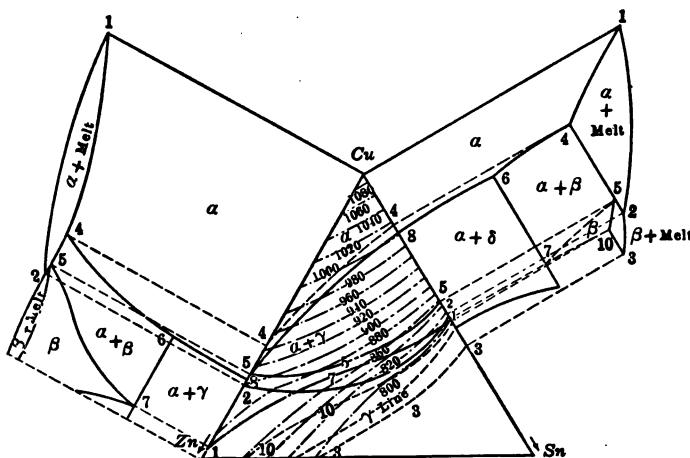
Fig. 22.—Part of the copper-tin-zinc constitution diagram.

The solidification of other alloys of this system can be followed by means of this diagram in the same way.

Another simple case is that of complete solubility of the three metals in both the liquid and solid states. Here we would have but one liquid and one solid phase with a liquidus surface and a solidus surface separating them. Between the two surfaces the alloys are part solid and part liquid. The compositions of the two phases must lie along the two lines determined by the intersection of the horizontal temperature plane and the two surfaces, but conjugate compositions would have to be determined by experimentation.

If the binary pairs are partially soluble in the solid state, the

ternary diagram will show small fields at the three corners, while the liquidus surfaces, as before, will intersect along the three binary eutectic lines and at the ternary eutectic point. The three solid phases separating out of the ternary eutectic will be the three saturated solid solutions.

We may take, as an example of a ternary system showing a peritectic reaction, the copper end of the copper-tin-zinc system which was blocked out by the author.[1] The diagram is shown in Fig. 22. We shall assume, for the sake of simplicity (what at the time was considered to be the fact) that the eutectoid reaction is continuous across the diagram. The contour lines drawn to show the liquidus surface are plotted from actual temperature measurements of the melting points. The lines bounding the α and the $\alpha + \gamma$ fields were determined by microscopical examinations of alloys of various compositions lying along and on both sides of the boundary lines.

[1] HOYT, *Journal* Inst. Metals, 1913, No. 2, p. 235.

CHAPTER II

THE PREPARATION OF METALLIC ALLOYS

In the present discussion we shall consider only the laboratory preparation of alloys and principally the method of fusion in a crucible, which is by far the commonest method used. Other methods, such as that of subjecting the component metals to pressure, cementation, electro-deposition, etc., will be considered when the occasion arises.

REFRACTORIES ·

On account of the high temperatures used in metallographic work and the necessity for using materials which will not seriously injure the melt, it is necessary to select the refractories with great care. As a guide in this selection, the more important refractories used are briefly considered.

1. Fire Clay.—Fire clay is one of the commonest refractories used in the manufacture of crucibles and furnace linings. Fire clays are principally mixtures of silica and alumina, SiO_2 and Al_2O_3, with non-fluxing impurities such as CaO, MgO, etc. Total silica and alumina run above 80 per cent. Fire clay crucibles are used in common practice for melting down iron and steel and most of the more fusible metals and alloys, while the metals with higher melting points require a more refractory material. Fire clay is, for most purposes, chemically inert, particularly when it is used at the lower temperatures, but at high temperatures secondary reactions may take place and introduce impurities into the melt. A common reaction of this type is between carbon of steel and SiO_2 of the crucible which goes on continuously during the refining of crucible steel. In this way metallic silicon is introduced into the steel, which may or may not be desirable. To prevent contamination from such a source a more inert substance, such as magnesia, should be used.

2. Carbon.—Among the carbon refractories or those using carbon as a base come graphite, pure carbon, and certain carbonaceous materials mixed with alumina or fire clay as a bond, such

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as plumbago.   The carbon is useful both on account of its infusibility and because it produces a slightly reducing atmosphere. Graphite is the most suitable form of carbon which is used for this purpose since it is very dense and oxidizes but slowly. Another advantage possessed by these refractories is that they are excellent conductors of both heat and electricity and can be used as an integral part of the heating device.

Many metals such as manganese, tungsten, nickel, and others with high melting points, absorb carbon so that the use of this class of refractories is prohibited in the very field in which its infusibility would give it a very decided advantage over other refractories.   If a fire clay bond is used in the crucibles, the melt is further liable to contamination from the silicon.   The lining of graphite or plumbago crucibles to circumvent such difficulties will be discussed later.

A convenient form in which graphite may be purchased is as rods or electrodes, from which crucibles, tubes or spirals can be turned.

3. Aluminum Silicate.—Among the refractories using aluminum-silicate as a base, are porcelain, Marquardt mass, and one more recently developed by the Bureau of Standards, known as usalite.[1]

Porcelain is obtained by burning kaolin with feldspar and quartz.   The surface may or may not be glazed over.   Porcelain can be used at temperatures up to 1600°C., and Marquardt mass, which is a special mixture, up to 1700°C.   The silica of porcelain and Marquardt mass is reduced under certain circumstances so that these materials should be used guardedly.

Usalite is supposed to be a substitute for Marquardt mass. The following information is advanced by the makers.   It will withstand continuous exposure to temperatures exceeding 1650°C.   The glazed surface is chemically inert and is impervious to gases.   Usalite tubes are strong and somewhat flexible; in fact, they are not absolutely rigid even when cold.   The resistance to rapid changes in temperature is unusually high for porcelain.

It is important to remember that only the glazed porcelain is impermeable to gases and it is, only so long as the glaze remains intact.   On the other hand, the glazed is more fusible than the unglazed porcelain, so that unless the material is to resist chem-

[1] Made by the Stupakoff Laboratories, Pittsburgh, Pa.

ical action or hold a vacuum the unglazed porcelain is preferred. Ordinary porcelain cannot stand sudden changes of temperature.

4. Silica or Quartz.—There are two grades of refractories made of pure silica, one known as "fused silica," which is opaque, and the other known as "quartz glass" which is transparent and comparatively expensive. Quartz glass is made into apparatus of all descriptions similar to ordinary glass. It is very dense and refractory so that a high vacuum can be held, even at high temperatures. The most unusual property of quartz glass is its temperature coefficient of expansion, which is practically zero, so that it can undergo the most rapid changes in temperature without injury.

If quartz glass is used for too long a time at high temperatures it becomes devitrified and, on account of the change in volume which accompanies this change in state, the material cracks and splits off. Quartz is used for furnace tubes[1] and as a protective material for thermocouples. It is especially suitable for the latter as it can be thrust into a melt without harm and, also, because being impermeable to gases, it can be used with thin walls.

Fused silica is a much less expensive form of silica but it possesses the desirable properties of resistance to high temperatures, low coefficient of expansion and impermeability. Its melting point is between 1700°C. and 1800°C. but it softens at about 1500°C. and should not be used at higher temperatures. Fused silica has come to be one of the favorite refractories for pyrometer tubes. In this connection it should be remarked that fused silica is readily ruined if it comes in contact with metallic oxides, especially copper oxide and iron oxide.

5. The Alumina-silica Series.—Among the refractories of this class are alundum, bauxite, and alusil. These differ from the fire clays in that they contain a great excess of alumina; in fact the one most commonly used, alundum, is pure alumina with a small amount of fire clay as a bond.

Articles of alundum are made as follows: Bauxite, or practically pure alumina, is fused in the electric furnace, crushed, mixed with a bond, formed into shape and burned at a high

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[1] The special tube furnace of Rosenhain for quenching experiments has a quartz glass tube. Cold water may be admitted to the hot interior without causing any harm. See Rosenhain, *Jour.* Iron & Steel Inst., 1908, No. 1, p. 87.

temperature. In this way are made electric furnace cores, muffles, crucibles, and parts for the construction of electric furnaces, where the high thermal conductivity becomes an advantage. The melting point of alundum is given as approximately 2100°C. so that it can be used for melting platinum and other highly fusible metals. Alundum has a low coefficient of expansion so that it is not greatly affected by sudden changes in temperature. Alundum is not easily reduced at high temperatures and can be used for fusions of iron and steel. Alundum cement can be used as an inside coating of graphite crucibles for the electric melting of iron and steel alloys. It seems to be practically impossible to work with thick walled alundum crucibles without cracking. Thin walled crucibles are very much more satisfactory and are particularly useful for making fusions of small steel buttons in the electric vacuum furnace, in which case a slag protection is not required.

6. Basic Refractories.—The principal basic refractory used in metallographic work is magnesia, especially that which has been calcined in the electric furnace. Electrically calcined magnesia is less liable to crack and does not absorb carbon dioxide gas as does the ordinary magnesia. Magnesia has a very high melting point and is not easily reduced so that it can be used in the preparation of alloys which would reduce silica or absorb carbon from the ordinary crucibles. In this respect it is especially useful in the preparation of iron and manganese alloys. Magnesia will not hold a vacuum and cannot withstand rapid temperature variations. One of its chief uses is as a brasqueing material for other crucibles such as graphite and plumbago. For this purpose finely ground magnesite is mixed with a somewhat coarser ground magnesite and moistened with water or, better, with a magnesium chloride solution. The crucible is lined with this material and allowed to dry for several days. It is then put in an air bath and the temperature raised to 300 or 400°C. until the crucible and lining are thoroughly dry. It is now ready for use and can be introduced at once into a hot furnace.

Magnesia crucibles are smooth, homogeneous, and strong, and are almost indispensable in certain lines of metallographic work.[1] Magnesia can be used as a casing for thermocouples but only if no dangerous gases are present. At times the thermo-

[1] See G. WEINTRAUB, *Met. & Chem. Eng.*, 1912, Vol. 10, p. 308.

couple is protected by placing it within a platinum tube and the platinum tube in turn being protected by a magnesia casing.

OXIDATION AND CONTAMINATION OF THE MELT.

The best means of protecting an alloy from oxidation and the absorption of impurities during fusion is to melt in vacuo, in a crucible which is chemically inert. In the author's laboratory the Arsem furnace and thin walled alundum crucibles have given complete satisfaction. Ordinarily the metal or alloy is melted under a protective cover of some kind, such as a salt bath or a layer of finely ground carbon. Hanemann gives the following compositions for heating baths which have given good service.[1]

Salt baths:

250°– 550°C	1 $NaNO_3$ + 1 KNO_3
550°– 700°	4 $BaCl_2$ + 3 KCl + 2.5NaCl + 2 $CaCl_2$
680°–1000°	2 KCl + 1 $BaCl_2$
1000°–1300°	$BaCl_2$

These salt baths are melted down and brought to the desired temperature. The metals, when added, sink to the bottom of the crucible and melt down without oxidizing. Borax glass is also used as a protective cover for copper and the copper alloys.

Another method of preventing contamination of the melt is by passing an inert gas over the melt. The gas should be one which does not enter into chemical reaction with, and is not absorbed to any extent by, the melt. As the principal chemical action to be eliminated is oxidation, a reducing gas such as hydrogen, nitrogen or carbon monoxide is generally used. Before being passed into the furnace the gas should be purified (removal of the oxygen) by passing it through an alkaline solution of pyrogallic acid or a tube containing glowing copper, and dried by means of sulphuric acid.

In Table 1 is given a list of the crucibles, covers and atmospheres which have been used in the preparation of alloys of the common metals. The table is essentially the same as that given by Guertler in the International Journal of Metallography, 1913. Vol. 4, p. 328. The table is to be used in the following manner.

If an alloy of two or more metals is to be made, the crucible, cover and atmosphere are chosen which will best suit the greatest

[1] See HANEMANN, "Einführung in die Metallographie und Wärmebehandlung," 1915, p. 116.

TABLE 1

Metals	Crucible	Cover	Atmosphere
Aluminum...	Porcelain (if mixed with other metals). Jena glass (with rapid manipulation; best lined with magnesia). Fire clay crucibles (are attacked more or less; may be used if mixed with sufficient other metals).	Powdered graphite. KCL & NaCl or NaCl (may also be melted without cover).	Hydrogen. Nitrogen. Oxygen is dangerous.
Copper......	Graphite. Carbon. Graphite. Porcelain. Aluminum. Silica.	Powdered graphite. KCL with NaCl. BaCl₂. Sea salt dissolves the oxides present. B₂O₃ and borax also dissolves oxides. KCN. Gypsum. Granulated carbon. NaCl.	Hydrogen, in presence of many metalloids. Nitrogen, better than hydrogen. Carbon dioxide. Illuminating gas. Illuminating gas flame.
Gold........	Any non-metallic crucible can be used.	Same as silver.	According to choice, preferably oxidizing.
Iron........	Porcelain is very satisfactory; also well to use magnesia lining. Magnesia. Silica. Magnesite. Carbon. (The melt absorbs carbon from carbon or graphite crucibles but these may be used if lined with magnesia.) Marquardt mass. Alundum.	Barium chloride. (Sea salt dissolves the oxides.) Sodium nitrate with manganese dioxide. Gypsum. Granulated carbon is not to be used. Acid or basic slags.	Hydrogen, Nitrogen (better avoided as it nitrates iron).
Lead........	Graphite and carbon.	Borax. KCN. Glass (at high temp.). Granulated carbon. (May also be melted without cover.)	Hydrogen. Nitrogen and carbon dioxide.
Nickel......	Same as iron.		Hydrogen. Nitrogen.
Platinum....	All non-metallic crucibles are satisfactory except carbon which is better avoided.	Glass.	None necessary
Silver......	Nickel crucibles. Iron crucibles. Fire clay. Carbon. Porcelain.	Potassium chloride. Sodium chloride. Potassium cyanide. Borax. (In the presence of metalloids without cover.)	Carbon dioxide. Illuminating gas.
Tin.........	Same as lead.		
Zinc........	Jena glass. Graphite. Silica. Fire clay.	Borax. Potassium chloride. Sodium chloride. Ammonium chloride. Zinc chloride (used commercially). Granulated carbon. (Can be melted without cover.)	Nitrogen. Illuminating gas.

number of metals. If one metal is in great excess, the conditions should be chosen to suit that metal. While in most cases it is immaterial which of the covers suggested is used, still it is often necessary to select a cover which will not react with the crucible. Graphite crucibles are recommended for copper and potassium cyanide is recommended as a cover, but they should not be used together. Another point of importance is the selection of the neutral atmosphere. If the gas diffuses readily through the crucible, it is obvious that the cover will be of little assistance to the melt. Porcelain and magnesium crucibles are recommended for melting iron and iron alloys. As hydrogen diffuses readily through porcelain and still more so through magnesia it would be quite useless to use a cover with such a combination.

Deoxidation.—Impurities, first of all, should be prevented from entering the melt by a judicious selection of crucible, cover, and atmosphere. These points have already been touched upon in the above discussion.

If impurities are present, they can usually be removed by fluxes or deoxidizers, such as small amounts of aluminum, silicon, or phosphorus. An example will serve to illustrate the action of a deoxidizer. Commercial copper and copper which has been carelessly melted by exposing it to the action of the air, is always contaminated with a certain amount of copper-oxide. If deoxidized copper is desired, phosphorus, either pure or in the form of a phosphor-copper, can be added to the melt to combine with the oxygen and remove it from the molten copper. The amount added should be just slightly in excess of the amount necessary to reduce the copper-oxide.

Aluminum has a high heat of combustion so that it too is an efficient deoxidizer. It is used in the preparation of copper, iron and other alloys. If the melt is badly oxidized the aluminum should be added in small amounts so as to prevent a too sudden rise in the temperature. This rise in temperature was formerly considered to be due to the great heat of formation of the aluminum alloys.

Table 2 gives the heats of combustion of the metals to their oxides. The heat of combustion gives the quantitative value of the ability of any metal to act as a deoxidizing agent. Theoretically any metal of this table will deoxidize the oxide of a metal coming after it and its oxide will, in turn, be deoxidized by any metal preceding it. This table makes it clear that carbon, in the

form of a carbon stirring rod, can be used to deoxidize the melts of many of the common metals. This table does not hold, necessarily, for all temperatures; reactions may occur which actually reverse the process. An example of this is to be found in the well-known action between carbon and silica at the high temperatures of the electric furnace when the oxide SiO_2 is actually reduced in the presence of carbon.

TABLE 2

Metals	Heat of combustion, calories	Metals	Heat of combustion, calories
Magnesium (MgO)	145.5	Cadmium (CdO)	66.3
Lithium (LiO$_2$)	145.0	Iron ($\frac{1}{2}$ Fe$_2$O$_3$)	65.9
Calcium (CaO)	145.0	Tungsten ($\frac{1}{2}$ WO$_2$)	65.7
Strontium (SrO)	131.2 (?)	Cobalt (CoO)	64.5
Aluminum ($\frac{1}{3}$ Al$_2$O$_3$)	131.2	Nickel (NiO)	61.5
Sodium (Na$_2$O)	100.9	Hydrogen (H$_2$O gas)	58.1
Potassium (K$_2$O)	98.2	Antimony ($\frac{1}{3}$ Sb$_2$O$_3$)	55.6
Rubidium (Rb$_2$O)	95.5	Arsenic ($\frac{1}{3}$ As$_2$O$_3$)	52.1
Silicon ($\frac{1}{2}$ SiO$_2$)	90.9	Lead (PbO)	50.8
Boron ($\frac{1}{3}$ Bo$_2$O$_3$)	90.9	Bismuth ($\frac{1}{3}$ Bi$_2$O$_3$)	46.4
Manganese (MnO)	90.0	Thallium (Tl$_2$O)	42.8
Zinc (ZnO)	84.8	Copper (Cu$_2$O)	43.8
Phosphorus ($\frac{1}{5}$ P$_2$O$_5$)	73.1	Sulphur ($\frac{1}{2}$ SO$_2$ gas)	34.6
Tin (SnO)	70.7	Mercury (HgO)	21.5
Tin ($\frac{1}{2}$ SnO$_2$)	70.6	Silver (Ag$_2$O)	7.0
Oxide of carbon (CO)	68.2		

Volatilization.—Additional difficulties are encountered if one or more of the metals volatilize readily at the temperature at which the alloy is prepared. The easily volatile metals are zinc, cadmium, arsenic, and, of course, mercury. Zinc volatilizes above its melting point with increasing vehemence until at 920°C. it boils. This results in a partial loss of the zinc as fumes of zinc oxide or even in segregation. To keep the loss at a minimum alloys of zinc having a comparatively high melting point are prepared by first melting down the remainder of the alloy, whereupon the zinc is added in large pieces and quickly immersed with a stirring rod. Part of the zinc is unavoidably volatilized and oxidized, causing a loss which is at times as high as 4 per cent. This loss must be allowed for when weighing out the zinc. Zinc-rich alloys with melting points below 920°C. have been prepared by

melting the zinc first and dissolving the other metals in the melt, in which case the loss of zinc is quite small. Intermediate alloys containing about 50 per cent. zinc are frequently used in the preparation of other alloys, in order to minimize the loss of zinc.

Arsenic volatilizes more readily than zinc so that the same difficulties are encountered in the preparation of arsenic alloys as described above. A method of preparing arsenic-rich alloys in a small, evacuated and sealed thimble of procelain is given in the International Journal of Metallography, Vol. 6, Heicke.

Homogeneity.—Aside from minor segregation it is generally simple enough to produce homogeneous alloys by fusion. The principal difficulty is encountered where two phases are present (two melts or solid and melt), which differ appreciably in specific gravity and which, therefore, liquate. Alloys of lead are the chief offenders in this respect, because lead is insoluble in many of the other metals, either in the solid or the liquid state, and is at the same time considerably heavier. Here, vigorous stirring of the melt and chill casting in an iron mold, are usually resorted to in order to produce homogeneous alloys.

LABORATORY FURNACES

The amounts involved in metallographic laboratory practice are small (seldom above 300 grams, 100 grams being the average melt) so that only the smaller types of furnaces come into consideration. By far the majority of these are either gas or electric furnaces on account of the better temperature control, more even temperature distribution and general all-around efficiency, as compared with other types. In case larger amounts are to be made, as in the study of the mechanical properties of alloys, the large metal melting furnaces are used, as in commercial practice.

Gas Furnaces.—The numerous gas crucible furnaces on the market afford a wide variety in the choice of a suitable gas furnace for preparing metallic alloys. Among them are the following:

Méker Crucible Furnaces.—There are two types of Méker furnaces on the market, both of which use the well-known Méker burner. The small type, which operates on the principle of the Bunsen burner, is capable of melting down copper by using the natural draft. The larger furnace, for use with compressed air, is shown in Fig. 23, in which temperatures up to 1400° C. should be secured with sufficient gas pressure. The thermal in-

sulation and heat distribution of these furnaces are not such that they can be used for making freezing point determinations unless, as suggested by Desch, an extra insulation of asbestos board (transite board) is placed around them.
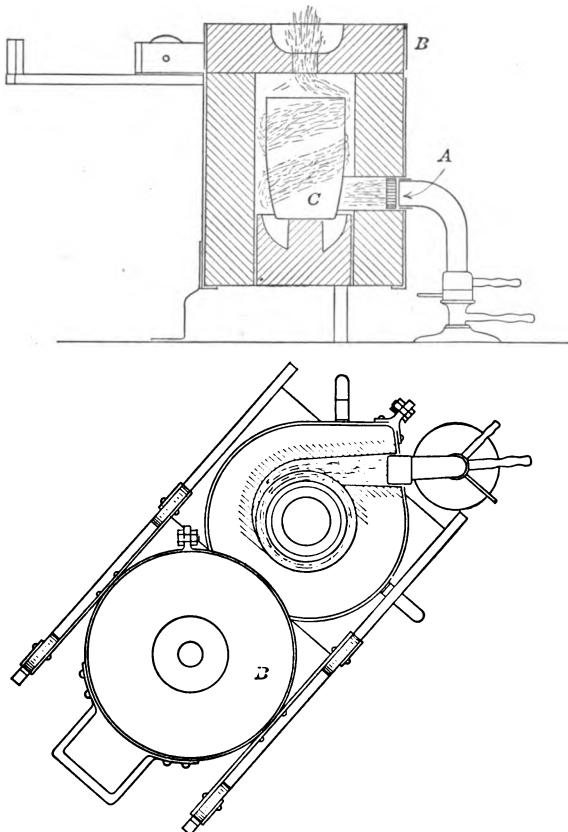
Fig. 23.—Méker furnace. *A*, burner; *B*, cover; *C*, crucible.

Fletcher's Crucible Furnace.—Another very convenient laboratory furnace for melting down small amounts of copper and metals with lower melting points is the Fletcher furnace. It uses compressed air and can be placed on any laboratory table, preferably on transite board. At the Bureau of Standards this furnace has been used with a pre-heater to melt down pure iron. In this case the furnace was extra lined with magnesia.

A surface combustion furnace has also been developed which is capable of producing temperatures above 1600°C. which is very

suitable for melting steel and alloys of the iron group. By replacing the air for combustion with oxygen and by using magnesia for the furnace lining, temperatures in excess of 2000°C. can be secured.

Gas furnaces are also extensively used in the heat treatment of metals and alloys. A combination of three furnaces such as is used at the Minnesota School of Mines is shown in Fig. 24. This set operates on gas and air under a small pressure which is
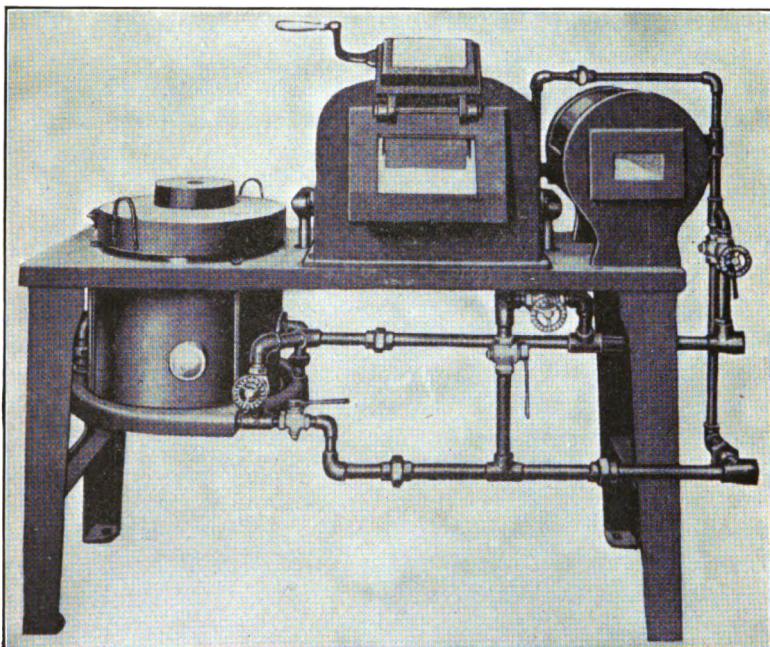
FIG. 24.—Gas furnace set. (*Chicago Flexible Shaft Co.*)

supplied from a small blower. This combination is useful for the following purposes: As a forge; for the heat treatment of high speed steel; for the annealing and heat treatment of steels and alloys, (*a*) in an open chamber, or (*b*) in a lead pot; and for the preparation of fairly large amounts of the more fusible alloys.

Electric Furnaces.—Electric furnaces are usually preferable to and are more generally used than gas furnaces in metallographic work, because:

1. The electric current offers a cleaner heating agent and is more convenient to operate at high temperatures.

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2. Greater variation in temperature and closer regulation are possible with electric furnaces.[1]

3. A more even temperature distribution within the furnace can be obtained.

4. The construction of the electric furnace facilitates the operations and makes it more convenient to make fusions in a vacuum or neutral atmosphere.

Tube Furnaces.—The "tube furnace," in which the heat is developed by passing a current through a resistance wire, is the most common type of furnace used in metallographic work. One of these of the Heraeus type is shown in Fig. 25. The resistor in this furnace is a wire or ribbon of platinum wrapped in the form of a helix on a tube of unglazed porcelain. The heat generated per second, expressed in calories, is equal to

$$0.2387 \times I^2R$$

where I is the current flowing in amperes and R is the resistance of the coil in ohms. The temperature produced by this amount of heat varies with the design and construction of the furnace. The tube is placed within an outer, and concentric, procelain tube which, in turn, is insulated on the outside by a thick layer of magnesia and an outer wrapping of asbestos. The current used (as measured by an ammeter) should never be greater than that marked on the furnace, on account of the danger of local overheating and burning out the furnace. In any case the temperature should not be raised above 1300°C. as at that temperature electrolysis, and consequent decomposition of the porcelain, sets in. If a silica tube is used in place of the porcelain, the temperature should be kept below 1000°C. at which temperature silica becomes a conductor. An additional precaution to avoid overheating is that of measuring the temperature within the furnace pyrometrically. Alternating current (either 110 or 220 volts) is to be preferred to direct current, which, if allowed to run continuously in one direction, affects the platinum coil. If direct current must be used, its polarity should be reversed from time to time.

Base metals such as iron, nickel and nickel-chromium alloys,

[1] Gas furnaces, if equipped with automatic thermostats (American Gas Furnace Co.), can be kept at a fairly uniform temperature. For the description of a pneumatic thermostat capable of maintaining the temperature in an electric furnace constant to less than 1°C. at 400°C., see HAUGHTON and HANSEN, *Journ.* Inst. Met., 1915, Vol. 14, p. 145.

are now used with satisfactory results for the lower ranges in temperature. The maximum safe working temperature depends on the "deterioration" temperature of the material, by which is meant the minimum temperature at which it fails due to the absorption of gases or impurities, oxidation, or even melting. It
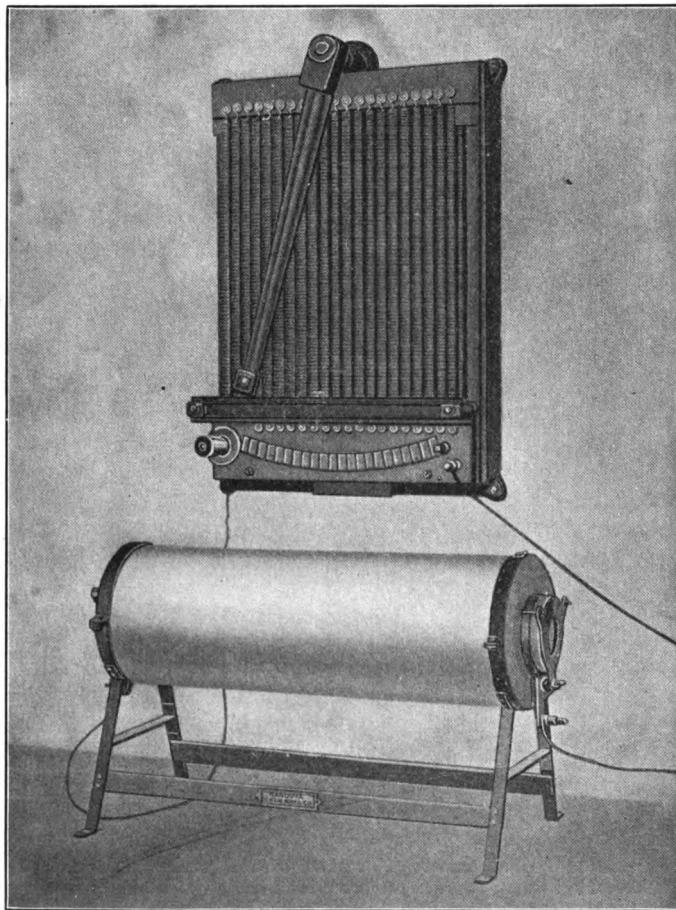
FIG. 25.—Platinum tube furnace with rheostat. (*Hanovia Chemical Company.*)

is possible to raise the normal deterioration temperature in certain cases; *e.g.*, iron wire commences to oxidize at 600°C., but, by eliminating oxidation, it can be safely used at considerably higher temperatures. Nickel wire can be used up to 900°C. but at higher temperatures it absorbs impurities and becomes too

brittle for continued service. Nichrome alloys, such as "chromel,"[1] can be used up to 1300°C. Tungsten and molybdenum are now used up to 1700°C. but hydrogen gas must be passed through the furnace to prevent oxidation.
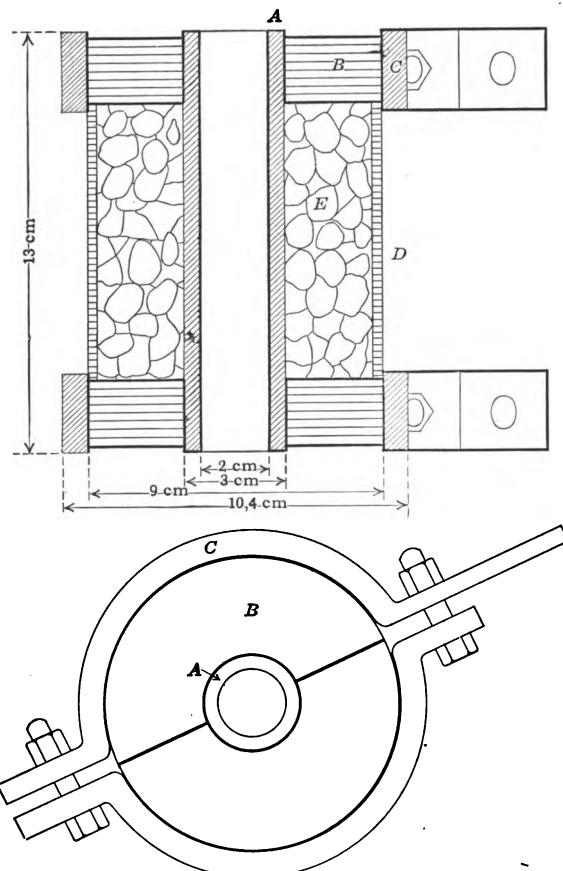
Fig. 26.—Carbon tube furnace. *A*, carbon tube; *B*, carbon split rings; *C*, brass electrode rings; *D*, outer tube; *E*, insulating material. (*Ruer.*)

It is comparatively easy to construct a tube furnace in the laboratory using a tube of porcelain, alundum, or quartz, and a heating element of base metal or platinum or molybdenum. The data, such as the diameters of the wire, its specific resistance, etc., can be obtained from the manufacturers.

[1] The General Electric Co. and The Hoskins Manufacturing Co.

Carbon Tube Resistance Furnaces.—If a heavy current is available, a carbon tube can be used as a resistor, the current passing through the tube direct. This type of furnace as introduced by Tammann is shown in Fig. 26. The current required is greater than that of the ordinary circuit so it must be transformed in a transformer. In this manner current of 600–1800 amperes and approximately 10 volts is short circuited through the carbon tube in sufficient amount to heat the interior to any desired temperature. These furnaces are usually quite small and are principally used at temperatures above 1500°C. to prepare melts of the highly refractory metals. Since there is no danger of hurting the furnace by rapid heating, a heavy current may be passed through the cold furnace sufficient to raise the temperature to 1500° in a few moments. The crucibles used are of porcelain, Marquardt mass, alundum, magnesia, or other refractory material, closed at one end and long enough to project above the furnace proper. The upper end is closed by either a metallic stopper or a fire clay plug, which is pierced to allow the insertion of a stirring rod or a pyrometer for measuring the temperature inside the tube, or for admitting neutral gases or evacuating the furnace.

The temperature range for a well constructed furnace of this type is from 300° C. to about 2000° C. At high temperatures there is a continual oxidation of the carbon in the resistor forming carbon monoxide. On this account the tube deteriorates and must be renewed after about twenty hours use. The first time one of these furnaces is put in operation the temperature should be rasied very gradually and held at about 1000° C. until all volatilization ceases. After this treatment there is no danger from rapid heating.

A more satisfactory material than carbon for the resistor is iridium, but as iridium is very expensive its use is limited to the larger laboratories.

Kryptol or Granular Resistance Furnaces.—A furnace using granular carbon as a resistance is shown in Fig. 27. The current passes between the two iron electrodes, *B*, through the bed of granular carbon marked *A*; *D* is a tube of refractory material and *C* is the crucible containing the melt supported on the base *U*. These furnaces can be constructed in sizes varying from two inches to four or five inches in internal diameter and up to three feet in height. They are used chiefly to melt down the more

refractory metals and alloys in comparatively large quantities. The temperature range is from about 400° C. to 1800° C. The carbon must be finely ground to give high temperatures and well
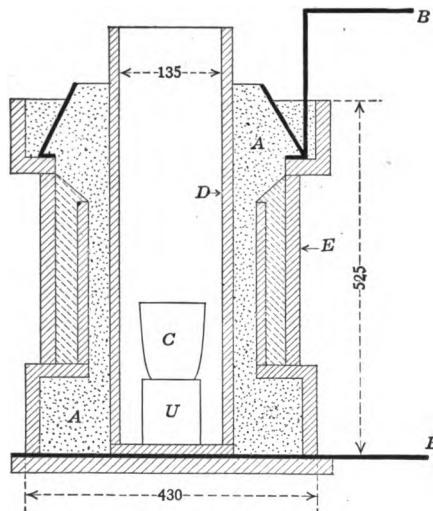
FIG. 27.—Granular resistance furnace.   A, granular carbon; B, iron electrodes; C, crucible; D, refractory tube; E, fire clay; U, support.   Dimensions are in millimeters.   (Goerens and Ruer.)
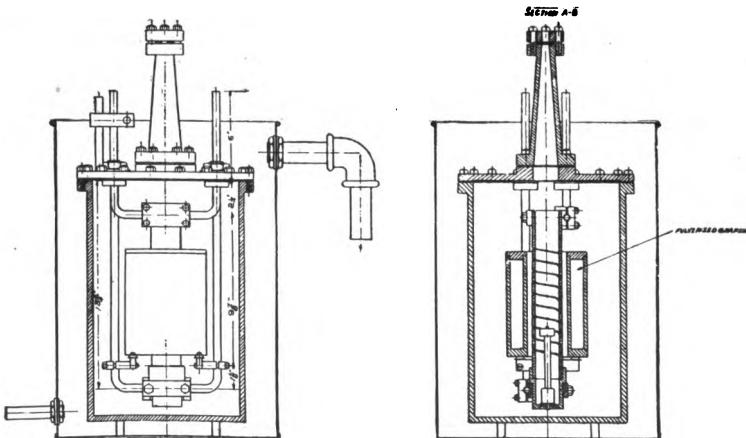
FIG. 28.—Arsem vacuum furnace—small vertical type.   (General Electric Co.)

packed to prevent local arcing and overheating.   Furnaces using a bed of finely ground carbon, or a mixture of finely ground carbon and carborundum, and various silicates (called kryptol),

are made in various forms, too numerous for detailed description here.[1]

A vacuum furnace as constructed by the General Electric Company, is shown in Fig. 28.[2] The heating device is a carbon helix constructed by cutting a helical slit in a tube of hard carbon. The design of the heating element depends on the current available but it works best with a transformer giving a range in voltage from 15 to 60 volts. The furnace and electrodes are necessarily water cooled. The crucible containing the melt is supported on a graphite rod and comes at the center of the heated space. The degree of exhaustion required is fairly high but can be readily maintained with a two stage, oil sealed vacuum pump such as is used for exhausting electric lamps. The writer has used this furnace for a number of years in the preparation of buttons of iron, steel and alloys of high melting point, particularly in case it was desired to eliminate the effects of gases.

[1] For descriptions of these furnaces see FRIEDRICH, *Met.*, 1908, Vol. 5, p. 703; MATTONET, *ibid.*, 1908, Vol. 5, p. 186; DEKERT, *ibid.;* HARKORT, *ibid.*, 1907, Vol. 4, p. 617; SIMONIS, *Stahl u. Eisen*, 1907, p. 739. For the construction of a very convenient split tube furnace according to HANE-MANN, see *Stahl u. Eisen*, 1911, p. 334.

[2] *General Electric Company, Bulletin* No. 49711. A similar furnace has been described in *Met.*, 1909, Vol. 6, p. 145. See also OBERHOFFER, *Met.*, 1907, Vol. 4, pp. 427, 447, and 486; *ibid.*, 1908, Vol. 5, p. 173; and RUFF and GOECKE, *ibid.*, 1911, Vol. 8, p. 417.

CHAPTER III

METALLIC MICROSCOPY

The microscope, offering the most direct means of observing the physical character and constitution of metals and alloys, facilitates as well the determination of many points which are of great technical importance, such as grain size, and the heat and mechanical treatments to which the materials have been subjected. For both scientific and technical reasons, the microscopical examination of metals and alloys has been pushed with exceptional zest and this study can truly be regarded as the most important branch of metallography.[1]

Sorby and Martens, who were first in the field of metallic microscopy, recognized at once the necessity of examining metals by reflected rather than by transmitted light, as is done in the case of biological and petrographical subjects. For this purpose they developed the technique of preparing "microsections," which is essentially the same as is used today.

Preparation of Microsections.—Microsections for the microscopical examination of metals are samples of the piece to be examined, prepared with one plane surface polished free from scratches.[2]

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[1] In certain quarters, even today, metallic microscopy is regarded as the single pursuit of metallography, as was given by OSMOND in his original definition. In view of the present scope of the scientific study of the metallic alloys, this definition of metallography is too limited to be of further use.

[2] The technique of the preparation and microscopical examination of metals is discussed from time to time in the technical journals. The articles bring out the different ways in which this can be done and they are instructive to anyone considering taking up this work. Such a contribution is the paper by PROFESSOR BOYER on "Microscopic Metallography and Its Use in France," *Eng. Mag.*, 1908, Vol. 36, p. 654. These points are also considered in the leading texts on metallography, such as DESCH, SAUVEUR, ROSENHAIN, OSMOND and STEAD, etc. Some early papers on metallic microscopy are:

MARTENS, *Zeit.* Ver deut. Ing., 1878 and 1880.
WEDDING, *Journ.* Iron & Steel Inst., 1885, No. 1, p. 187.
SORBY, *Journ.* Iron & Steel Inst., 1886, No. 1, p. 140.

Sampling.[1]—Taking the sample for the microsection, like the taking of the sample for chemical analysis, is the most important step in the entire examination, for on this depend the value and integrity of the conclusions drawn. The sample chosen must be truly characteristic of the specimen it represents, its size and location depending on the size and nature of the specimen and the purpose of the examination. A regulus or button, as prepared in the laboratory, is best examined by means of a section along the vertical axis. This exposes a cross section which will permit a detailed examination of all parts of the button. A profile, such as a channel or rail section, is usually sampled by means of a transverse section about $\frac{1}{2}$ to $\frac{3}{4}$ inch in thickness, from which can be made a macroscopic examination for flaws and segregations or a more minute microscopic examination for grain size, microconstituents, etc. If the case is that of a failure, a longitudinal section is also taken in order to compare the structure at the fracture with that some distance away. Slag inclusions and the effect of mechanical work on the structure can be studied better on a section taken parallel to the direction of working. In technical practice longitudinal sections are generally to be preferred to transverse sections.

Large sections, if too heavy and unwieldy for examining with delicate instruments, must be cut up into several small pieces, of which one or more may be taken to represent the whole. Wire, or other specimens of small cross section, are cut up into short pieces, wired into a bundle and the composite cross section examined. A small wire can be forced into a hole drilled in a small piece of steel and snipped off flush, whereupon it is ready for further treatment. Small specimens are at times fused into an alloy of low melting point, such as Wood's or Rose's metal, so that the specimen comes at or near the surface, whereupon any section desired may be taken. In the operations of grinding and polishing, the edges of the microsection are unavoidably more or less

SORBY, *Journ.* Iron & Steel Inst., 1887, No. 1, p. 255.

OSMOND, *Annales Mines*, 1885 (VIII) 8, p. 1.

MARTENS, *Stahl u. Eisen*, 1882, No. 2, p. 423.

WEDDING, *Stahl u. Eisen*, 1886, No. 2, p. 633.

STEIN, *Stahl u. Eisen*, 1888, No. 2, p. 595.

BAYLES, *Trans.* Amer. Inst. Min. Eng., 1882–3, Vol. 11, p. 261.

[1] For a more detailed discussion, see BAUER and DEISS, "The Sampling and Analysis of Iron and Steel," 1915.

rounded off.   To permit the examination of the edges, the section can likewise be embedded in a low fusing alloy.[1]

The first operation of taking the sample for the microsection is that of sawing off a piece of suitable size in a mechanical hack saw.   To be satisfactory for this work the saw should have a stroke of at least six inches and be able to accommodate sections up to five inches in diameter.[2]   A simple milling machine with a circular cutter is also very satisfactory for this work.

Hand hack saws may be used, but unless the operator is very skilful the surface will be left uneven and not as well suited for subsequent operations.   Some materials such as manganese steel, white cast iron, etc., must be cut with a diamond saw or thin emery disc or by means of an old hack saw blade with diamond dust and water.   Some specimens are too small to be conveniently held in the jaws of the machine; if so they should first be clamped in a small hand vise (using wooden backings if necessary), which in turn is held in the jaws of the machine.   The samples, when sawed off, should be marked for identification.

If the manipulation has been carefully performed the surface will be approximately plane but more or less deeply scratched. It is next in order to remove these scratches (as well as the superficial layer of "flowed metal") by means of coarse and fine grinding, keeping the surface as nearly plane as possible all the while. The coarse scratches can be removed on an ordinary machineshop bench grinder with emery or carborundum wheels.   This operation is preferably done under a stream of water to prevent heating the specimen.   Grinding the specimen again on coarse emery paper serves to true up the surface of the specimen and to eliminate any uncommonly deep scratches.   This may be satisfactorily and conveniently done on an iron disc on the opposite end of the bench grinder, on to which the emery paper is glued.

A file or set of files held horizontally in a vise is also used at times in place of the bench grinder, but should hardly be used if an emery wheel is available, not only because the use of files is inconvenient, but also because they are more apt to tear the sur-

[1] See CAMPION and FERGUSON, "On a Method of Preparing Sections of Fractures of Steel for Microscopic Examination," *Journ.* Iron & Steel Inst., 1913, Vol. 88, p. 385 and the discussion.   The present writer has found that sealing wax can be used as an embedding material in many cases, using a brass ring, or even a steel nut, as a supporting frame.   The dissolving action of alcohol on the wax is a disadvantage here.

[2] Larger sections are sawed off on a large hack saw or on a band saw.

face of the specimen. If it is not necessary to examine the outer surface of the specimen, the edge may be slightly beveled to prevent tearing the polishing cloth by the sharp corners. Extremely hard and tough specimens can be worn down by diamond dust or emery powder in water on a steel disc which rotates horizontally.

Fine Grinding.—The next step in the preparation of the microsection is that of fine grinding. The emery paper used for this purpose (as supplied by Hubert, France) usually comes in six grades, from the coarsest to the finest, 2, 1, 0, 00, 000, 0000. The specimen is ground on each paper in a direction at right angles to that used on the preceding paper, and in each case the grinding should be kept up until the scratches from the previous paper are removed.[1] As a rule the 000 paper is sufficiently fine for the final operation. The specimen should be grasped lightly but firmly by the tips of the fingers and held against the paper by a light pressure. The specimen should not be held fast in the fingers as there must be enough "give" to allow the surface of the specimen to seek the plane of the emery paper.

In former years fine grinding was done largely by hand on emery paper held on a plane piece of wood or on a glass plate. At present it is done by machine which, in most cases, does the work in less time and much more conveniently. The machines used at the Minnesota School of Mines are slow speed (600 r.p.m.) induction motors mounted on a heavy table. The armature shafts are extended through the motor housing and threaded to take an 8-inch disc face plate. The disc is screwed on flush against a heavy collar.[2] A circular disc of emery paper, Hubert brand, is pasted on to the face of the disc and rolled down flat with a photographer's roller. These discs offer large and unobstructed grinding surfaces and have proven very satisfactory for this work. The specimen is always placed on the disc at the center, where the linear velocity is negligible, to prevent cutting irregular facets on the surface, and then brought immediately to the outer edge for the grinding. Obviously it is a decided

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[1] A small hand lens aids materially in detecting the cross-scratches.

[2] In works practice one machine (also belt driven) can be used for all the grades of emery paper by making the face plates interchangeable. Many metallographers, especially in England, prefer horizontal discs and automatic specimen holders. This type of grinding machine is specially constructed and can be bought of scientific instrument makers. For descriptions of special metallographic grinding machines, see PRIMROSE, "Practical Metallography," p. 91.

advantage to have the grinding surface free of obstructions such as lock nuts and washers that are at times used to hold on the discs.

Polishing.—After the specimen has been ground on the finest paper (the 000 or the 0000, as the case may be) it is ready for polishing, the final step in the preparation of the microsection. Polishing is done on a piece of broadcloth (good grade) which is moistened with a mixture of polishing powder and water. This should be continued until the fine scratches from the last emery paper are removed. Then the section is washed in tap water and placed in a small dish of absolute alcohol to remove the water and to cut any grease from the surface.[1] After a few moments it is removed, dried in a blast of air and placed in a desiccator, to preserve the polished surface.

Polishing, like fine grinding, is now done by machine. The polishing machine need not be different from the fine grinding machines, except that the polishing disc is made of hard rubber and faced with broadcloth. It is housed in a metallic hood to carry off the water.

The polishing machine used in the School of Mines laboratory has a horizontal disc, driven through a bevel gear by a small motor. The specimen is held on the disc very lightly to avoid causing too serious flowage of the surface material. The specimen is also moved on the disc in the opposite direction to that of the rotation of the disc, so as to describe a circle or an e lipse. Another vital point to be considered here is the tenuity of the polishing solution. This must be sufficient to give complete mobility to the individual grains of the powder. Anything like a paste gives poor results. There are also other satisfactory polishing machines which are, in nearly all cases, very similar to the grinding machines, and need not be considered here.

To avoid scratching the specimen during this operation, it is desirable to locate the polishing machine in a separate room, one which is as free from dust and dirt as possible. If no such room is available, the polishing disc can be made interchangeable with the grinding discs of the grinding machines described above.

The principal polishing powders used are jewelers' rouge and alumina. Of the two the alumina is the more generally useful, since it gives equally satisfactory results in a shorter time and does not color the section, as does rouge under certain circum-

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[1] Ether may also be used to cut the grease.

stances. Alumina is prepared by levigation and is known as 6-hour, 12-hour and 24-hour alumina, depending on the length of time allowed for settling in distilled water. The 6-hour alumina is a rapid polishing powder and is used on steel and other hard metals. Fine grinding can be discontinued at the 00 paper. Two ounces of the powder are taken for 100 ounces of distilled water. The 12-hour alumina is more comparable to jewelers' rouge and is generally to be preferred to the 6-hour. It is especially useful for the non-ferrous alloys such as brass, bronze, German silver, etc. One ounce of the powder is taken for 100 ounces of distilled water. The 24-hour alumina is very fine and therefore is used in special cases such as preparing sections for examination under high magnifications or for polishing soft alloys. Six-tenths of an ounce of the powder are taken for 100 ounces of distilled water. Certain alloys, such as those rich in lead, become tarnished if water is used for polishing, in which case the water should be replaced by alcohol or a thin oil.

Microscopic Examination.—In technical metallography the direct examination of the section without further treatment plays a very important rôle and is used for the study of colored constituents such as graphite in cast iron, or slag and manganese sulphide in steel. The main mass of the section appears quite structureless as a metallic mirror. If the structure of the metallic portion is to be examined it must be developed or brought out by some special method such as will be discussed in the following.

Development of the Structure.[1]—The structure of a metallic alloy can be compared to the image on an exposed photographic plate: in either case the structure (or image) is latent and must be brought out by suitable means. As the photographic plate is treated with a chemical reagent called the "developer," so is the microsection likewise treated with a chemical reagent, called the "etching reagent." The process of developing the structure by chemical means is called "etching." The specimen is first cleaned in absolute alcohol and then placed in the etching reagent which is contained in a small glass dish. The liquid is kept in gentle motion to promote uniform etching of the specimen. The length of time for this varies with the strength and tem-

[1] Reference should be made to the valuable papers by HUDSON, "Etching Reagents and Their Application," *Journ. Inst. Met.*, 1915, Vol. 13, p. 193, and GUERTLER, *Intern. Journ. Met.*, 1917.

perature of the etching reagent and the nature of the specimen.
It is much shorter if the specimen is being prepared primarily
for examination under a high magnification, where relief effects
must be avoided, than for examination under lower magnifica-
tions. As a general rule, a desirable strength for the etching
reagent is such that at least one to two minutes will be required
for etching. After a sufficient length of time to develop the
structure to the correct amount, the specimen is removed,
washed in a jet of water to remove the last traces of the etching
reagent, again placed in alcohol, and then dried in an air blast.
It is now either examined at once under the microscope or placed
in a desiccator while awaiting examination.[1]

The Action of Etching Reagents.—(1) On pure metals and
chemically homogeneous alloys consisting of only one constituent:
In considering the effect of lightly etching the polished surface
of a pure metal (or homogeneous solid solution) it must be borne
in mind that the microsection represents the end view of a cross
section of an aggregate of crystallites, all differently oriented.
The etching reagent corrodes the crystallites to different depths,
depending on their crystallographic orinetation, so that minute
terraces are left from one crystallite to the next. These terraces,
under the microscope, form a surface pattern similar to that
shown in Fig. 47[2] and bring out the structure of the metal.
This action will be treated somewhat more in detail in the next
chapter.

(2) On alloys containing two or more constituents: If an
alloy consists of two or more constituents, one of them is usually
electro-positive to the other, so that it alone is attacked by
the etching reagent—at least until etching is carried to quite
an extent. This develops the structure by outlining and slightly
roughening one of the constituents. If this constituent is colored
at the same time, the structure of the alloy is brought out with

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[1] Rosenhain gives a method of preserving microsections as follows: The
polished and etched section is coated with a fairly thick varnish made by
dissolving collodion in amyl acetate or celluloid in acetone. The coating
is sufficient to protect the specimens for several months and is still so thin
that the ordinary examination can be made without removing it. Speci-
mens of iron and steel can be rendered passive by placing them in a solution
of chromic acid, and so remain free from rust and corrosion.

[2] Some metallographers contend that the darkening of the crystal borders
is due to a more rapid dissolution of the material at those places which leaves
minute trenches.

exceptional clarity. It is noteworthy that etching, in this case, confines itself almost entirely to a differential corrosion or coloring of the constituents. Only after more prolonged etching are the boundaries of the crystallites of both phases made apparent.

Etching Reagents.—The following list gives the formulæ and uses of the common etching reagents which have been recommended from time to time in the literature. No list of this kind can be complete, but it will be sufficient if a metallographist (particularly a beginner) can get enough useful information here to enable him to compile and standardize the etching media which he finds of greatest use and convenience in his own work.

Concentrated Nitric Acid: Sp. Gr. 1.4.—Concentrated nitric acid is seldom used as an etching reagent. Sauveur recommends immersing the sample in concentrated acid, in which it immediately becomes passive, and subsequently spraying it with water. The dilute acid which is thus formed acts as the etching reagent. Concentrated nitric acid has been used to develop the structure of slag inclusions in certain iron alloys, as it acts on the slag but not on the iron.

Dilute Nitric Acid.—Nitric acid forms an oxide of the metal which is either soluble, slightly soluble, or insoluble in the dilute acid according to its concentration. If the oxide is soluble, it dissolves as rapidly as it is formed, in which case the surface is slowly corroded. If the oxidation proceeds at a greater rate than the solution, an oxide film is formed on the metal which produces interference colors. This is generally an undesirable etching effect and has led to the adoption of other and non-oxidizing reagents for most purposes.

Nitric acid is commonly used at various strengths dissolved in either distilled water or ethyl alcohol. One to 5 per cent. nitric acid alcohol is used to etch wrought iron, steel (annealed or heat treated), and cast iron, while the 10 per cent. is useful for manganese steel, nickel steel, etc. This solution is very serviceable for etching preparatory to determinations of the grain size. A 4 per cent. solution of nitric acid in iso-amyl alcohol was suggested by Kourbatoff (Reagent A) for etching both quenched and tempered steels. He also recommended the following solutions for the determination of troostite and sorbite in steel:

Reagent C,
>1 part of a 4 per cent. solution of nitric acid in acetic anhydride, 1 part methyl alcohol, 1 part ethyl alcohol, and 1 part iso-amyl alcohol.

Reagent D,
>2 parts of a saturated solution of nitrophenol and 2 parts of a 4 per cent. solution of nitric acid in alcohol.

These solutions color first the troostite and then the sorbite. The samples, after etching, should be washed in absolute alcohol in preference to the usual tap water.

A dilute solution of nitric acid in amyl alcohol is used extensively in commercial practice and is satisfactory for low powered examinations. This reagent attacks the slag and "oxide" inclusions and leaves the surface pitted. This effect serves as a rough test for the "condition" of the steel. It is too "coarse" in its action on annealed steel for high powered examinations.

Timofeef has suggested adding a few drops of a solution of 6 grams Cr_2O_3 and 94 grams nitric acid to 50 c.c. water for etching zinc.

Rosenhain suggests the use of nitric acid for the determination of lead and oxides in copper and brass, which are brought out as black inclusions. He also suggests dilute nitric acid in water (5 to 10 per cent.) for etching pure lead, alloys of lead and tin, type metals, and bearing metals.

Hydrochloric Acid.—Hydrochloric acid generally dissolves one constituent more rapidly than another giving a slight relief effect. Hanemann recommends the solution made by dissolving 1 c.c. hydrochloric acid (1.19) in 100 c.c. absolute ethyl alcohol for the iron-carbon alloys in both the hardened and annealed states.[1] A few cubic centimeters of a 5 per cent. solution of picric acid in alcohol is added to accelerate the action when etching nickel, chromium, and other special steels. Kourbatoff suggested the following solution for hardened steels:

Reagent B,
>4 parts hydrochloric acid,
>20 parts of iso-amyl alcohol and
>75 parts of a solution of nitroaniline or of nitrophenol in alcohol.

[1] Preuss advises against using HCl as it attacks the small pores of the metal and enlarges them into holes which do not represent the actual condition of the metal.

Le Chatelier suggested adding cupric chloride to the 10 per cent. solution in alcohol for etching steel, 1 per cent. for hardened, and 5 per cent. for annealed steels. Hydrochloric acid, both dilute and concentrated, is used for etching tin alloys.

Picric Acid.—Picric acid is perhaps the most commonly used reagent for the determination of the microconstituents of iron-carbon alloys. Variations in the rate of attack can be secured by using solvents giving different degrees of ionization. Such a series of solvents is water, methyl alcohol, ethyl alcohol, glycerine, propyl alcohol, amyl alcohol and iso-amyl alcohol in which the ionization, and therefore the chemical activity, decreases in the order named. Two solutions commonly used are:

1. Picric acid, 4 grams, in ethyl alcohol, 100 c.c.
2. Picric acid, 4 grams, in iso-amyl alcohol, 100 c.c.

The first solution attacks steel at a more rapid rate than the second. The specimens are, in each case, washed with absolute alcohol and dired.

Robin suggests the use of a concentrated solution of picric acid in alcohol for etching quenched steels, especially the high carbon steels. The specimen is allowed to remain in the solution from 30 seconds to one minute, or until the surface tarnishes to a brown or green in reflected light, whereupon it is removed and washed in water. Characteristic coloring effects are produced on austenitic and martensitic nickel, manganese and chromium steels, by which they may be distinguished. Picric acid is not serviceable for etching many of the special steels which require an oxidizing etching reagent, such as nitric acid, aqua regia or a mixture of sulphuric acid and chromic acid. Stead recommends adding a few drops of nitric acid to the picric acid for etching annealed steels.

Sodium Picrate.—Sodium picrate is used for the determination of the iron carbide, cementite, in steels when it occurs in sufficiently large particles. Only the relatively large crystals of cementite are attacked, so the etching brings out the "massive" cementite as black crystals on a light back ground of uncolored ferrite and pearlite. This etching reagent furnishes a sharp contrast to picric acid and hydrochloric acid which leave the cementite unaffected. The author has found sodium picrate very useful for etching ferrite plus martensite in quenched medium carbon steels. The etching requires several hours and brings

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out the martensite both by coloring it dark brown and by developing the characteristic structure.

Comstock recommends sodium picrate for distinguishing between manganese sulphide and iron oxide in steel.

Sodium picrate is made by digesting 25 grams of sodium hydrate and 2 grams of picric acid in 75 c.c. of water on a water bath for one-half an hour. The clear solution is decanted and preserved in air-tight bottles. The etching is always done at 100° C. over a water bath. The time required varies ordinarily from five to thirty minutes.

Tincture of Iodine.—The halogens which attack steel by separating the carbon are at times used for the examination of the iron-carbon alloys. The tincture of iodine was used successfully by Osmond but has given way to more convenient reagents. However, it is still commonly used to etch commercial shapes for the purpose of testing for segregation, etc., especially for macroscopic examination. The ordinary tincture or a solution of 1 gram of iodine in 20 c.c. alcohol can be used, applied with a brush. It is unnecessary to eliminate more than the coarser scratches for the macroscopic examination.

Copper Ammonium Chloride.—Copper ammonium chloride, as introduced by Heyn, is used principally for the development of the macrostructure of commercial sections of low carbon steel, with particular reference to phosphorus segregations. It is also used on wrought iron and white cast iron.

The solution is made by dissolving 10 grams of the double salt in 120 c.c. of water. The section to be etched is placed in a dish and covered with the solution which is allowed to act for sixty seconds. An electrolytic action, by which copper is deposited on the surface of the specimen, takes place, so that the solution is kept in gentle motion the entire time to insure uniformity. This deposit is wiped off with cotton under running water, after which the specimen is washed in alcohol and dried. If this dilution is adhered to there will be no difficulty in removing the deposit of copper.[1] The solution can be made up in stock quantities as it does not deteriorate. The white precipitate which forms from the commercial salt is harmless and does not need to be filtered off.

This reagent is not suitable for gray cast iron, quenched steel

[1] The addition of ammonia has been recommended when etching to obviate the necessity of removing the copper layer.

and the special steels as the deposit of copper cannot be easily removed. In high carbon steels, phosphorus, if present in the solid solution is colored brown, while the carbon-rich constituents which are also attacked by the reagent are colored a pure gray to black. This reagent is also recommended for "deep etching" to bring out the crystalline structure of pure metals, as in Fig. 49.

Basic Copper Ammonium Chloride.—A basic solution of the above salt is used for etching copper and many of the copper alloys, principally the brasses. It is prepared by adding ammonia to the standard solution until the precipitate, which forms, just goes into solution, giving a clear blue color. While this reagent is satisfactory for brass, the author has found Miller's reagent to be more satisfactory for the $\beta + \gamma$ brasses and probably so for the $\alpha + \beta$ brasses.

Ferric Chloride.—Heycock and Neville introduced ferric chloride as an etching reagent for the copper-tin alloys, but it is also used for etching various other of the copper alloys. A solution is prepared, according to Hanemann, by dissolving 4 grams of $FeCl_3$ and 30 c.c. HCl (1.12) in 1250 c.c. water.

Basic copper ammonium chloride and acid ferric chloride are both used to etch copper and the copper alloys, at times one, at times the other being more suitable. Hanemann and Merica made use of these two solutions in their work on the copper-aluminum alloys, on account of their reciprocal etching effect on the α, β, and γ constituents. The author has used both reagents for etching the Cu–Sn–Zn alloys but has found the basic copper ammonium chloride is better for the zinc-rich alloys and acid ferric chloride for the tin-rich alloys. Rosenhain suggests a stronger solution for use with the copper alloys, viz., $FeCl_3$ 10 grams, HCl 30 c.c., water 120 c.c.

Ammonia.—A dilute solution of ammonia in water is used to etch copper and its alloys, its effect being analogous to that of basic copper ammonium chloride and acid ferric chloride. At times a few cubic centimeters of hydrogen peroxide are added to increase the effect.

Ammonium Persulphate.—Law suggested the use of ammonium persulphate (10 per cent. solution of ammonium persulphate in water) for etching the copper alloys. A precaution, which must be observed in the use of this etching reagent, is treating the specimen with potash or soda to remove the grease, before etching.

This reagent is useful in developing the macrostructure of commercial copper and copper alloys.

Aqua Regia.—A solution of nitric acid 1 part, HCl 5 parts, and distilled water 6 parts, is used by Rose for etching gold, platinum and their alloys. Pure gold is etched sufficiently for oblique illumination in about one hour, at a temperature of 15°C.

Hydrofluoric Acid.—Brislee suggested the use of hydrofluoric acid (1 part fuming hydrofluoric acid to 10 to 20 parts water) for etching cast, worked, and annealed aluminum and its alloys. After etching, the specimen should be immersed in strong nitric acid, washed and dried. This reagent develops the grain outlines of aluminum.

Silver Nitrate.—A 5 per cent. solution of silver nitrate in water is useful for etching alloys of lead, tin, antimony, and bismuth, and the anti-friction alloys.

Sulphurous Acid.—Sulphurous acid, diluted with 25 volumes of water or alcohol, is used to etch hardened and tempered steels, cast iron, and irons containing manganese sulphide or phosphorus. By its use, the formation of cementite in tempered steels is made evident even when other reagents would fail to bring it out.[1]

Sodium and Potassium Hydroxides.—Sodium and potassium hydroxides are used in strengths up to 20 per cent. to etch aluminum alloys and zinc alloys. The practice at the National Physical Laboratory is to immerse the specimen for a short time in the reagent, rinse off in water, and then clean off the black deposit in concentrated chromic acid. A solution of 0.1 per cent. of sodium hydroxide in 50 per cent. alcohol is used at the Bureau of Standards to etch aluminum, particularly to bring out the impurities present.

Hydrogen Peroxide.—Jeffries recommends boiling hydrogen peroxide for etching tungsten and tungsten alloys.

Miller's Reagent.—Chromic Acid and Hydrogen Peroxide. A dilute solution of chromic acid is used, to which a few drops of hydrogen peroxide are added. The specimen is immersed and kept moving in the solution for a few seconds. It is then removed and washed immediately in running water. The addition of hydrogen peroxide causes a strong effervescence and turns the solution of chromic acid a very dark brown. If the

[1] See HILPERT and COLVER-GLAUERT, *Journ.* Iron & Steel Inst., 1910, No. 2, p. 54.

chromic acid solution is too strong, large gas bubbles are evolved which prevent uniform etching.

This reagent is equally satisfactory for all brasses and bronzes. In the copper-tin alloys the α does not stain while the δ remains a light blue; in the copper-zinc alloys the α is unchanged while the β remains light yellow as with ammonium persulphate, while in rolled brass the grain boundaries and twin crystals are brought out with great clearness. This reagent can also be used to etch silver. Miller has found this reagent particularly serviceable for developing the structure of brass welds for which a manganese brass containing no tin is used for the solder. This reagent is described in the *Journal* of the Institute of Metals, 1917, No. 2, p. 253.

Complex Reagents.—Cupric reagents have been developed for the purpose of bringing out the presence of impurities dissolved in ferrite of steel, principally phosphorus. Stead recommends the following reagent:

Cupric chloride	10 grams
Magnesium chloride	40 grams
Hydrochloric acid	20 c.c.
Alcohol to make up to	1000 c.c.

The salts are dissolved in the least possible quantity of hot water (about 10 per cent. of the whole). The microsection is covered with a thin layer and allowed to act for one minute, after which a second layer is added, etc., until the desired result is obtained. The composition of the reagent becomes adjusted to the particular sample being etched by the evaporation of the alcohol.[1]

A similar reagent, which seems to have certain advantages, was developed by Rosenhain and Haughton,[2] of the following composition:

Ferric chloride	30 grams
Hydrochloric acid (conc.)	100 c.c.
Cupric chloride	10 grams
Stannous chloride	0.5 grams
Water	1000 c.c.

This reagent, like the one above, attacks the phosphorus-free portions first, leaving the phosphorus-rich portions more or less unaffected.

[1] See STEAD, "Iron, Carbon and Phosphorus," *Journ.* Iron & Steel Inst., 1915, No. 1, p. 173.

[2] *Journ.* Iron & Steel Inst., 1914, No. 1, p. 515.

Le Chatelier developed a solution, similar to those of Stead, and Rosenhain and Haughton, for detecting phosphorus segregations in steel. Its composition is as follows:

Absolute methyl alcohol.................... 100 c.c.
Cupric chloride ($CuCl_2.2H_2O$).............. 1 gram
Magnesium chloride ($MgCl_2.6H_2O$).......... 4 grams
Concentrated hydrochloric acid............. 2 c.c.
Water.................................. 18 c.c.

These cupric reagents have proven to be extremely valuable for the estimation of phosphorus segregations in steel and their use is now standard metallographic practice. The method formerly employed was that of "heat tinting" developed by Stead. They possess the advantage over Heyn's reagent that they can be used for high-carbon steels and cast iron.

Mercury Chloride.—A solution of 10 grams mercuric chloride and 20 c.c. of hydrochloric acid (1.12) in 100 c.c. water is used in the macroscopic determination of sulphide enrichments in steel. This process is based on the fact that sulphur, present chiefly as iron sulphide and manganese sulphide, produces hydrogen sulphide with hydrochloric acid. A piece of fine silk is moistened with the above solution and placed on the polished surface of the sample. The sulphide inclusions generate hydrogen sulphide and precipitate black mercuric sulphide on the silk. The hydrogen sulphide which is given off causes small bubbles to arise under the silk cloth. These should be pressed down with a camel's-hair brush. This brush is used at the same time to renew the solution. The silk cloth is removed after four or five minutes and washed in water to remove the acid. This can be easily accomplished without disturbing the black mercury sulphide. The image produced on the silk cloth is a true negative of the sample, giving the sulphide enclosures. If the sulphur is present in a small amount and is uniformly distributed, the silk is colored a uniform gray.

Phosphorus produces hydrogen phosphide in dilute hydrochloric acid which precipitates mercury phosphide of a lemon-yellow color. There is little danger of confounding this deposit with the black mercury sulphide, especially as hydrogen phosphide is developed at a much slower rate than hydrogen sulphide.

Silver Bromide.—Silver bromide paper which has been soaked in a solution of 3 parts sulphuric acid in 97 parts water for a standard period of time, usually one minute, has been recom-

mended by Baumann for use in the same manner, to locate the sulphur segregations. The coloring produced is roughly proportional to the amount of sulphur present. This method is faulty in that phosphorus segregations also lead to a dark coloration under this treatment.

Electrolytic Etching.—A small electric current is used at times to assist in etching special steels and certain of the alloys. The specimen is made the anode and a piece of platinum foil the cathode in a 1 per cent. solution of HCl or H_2SO_4 or a neutral solution of ammonium nitrate or sodium thiosulphate. A current of about 0.5 amperes per square centimeter of the section is usually sufficient. Other electrolytes which are used are a 5 per cent. solution of sodium chloride, ammonia, and at times a solution of 1 c.c. HCl in 500 c.c. water. Le Chatelier recommends an electrolyte of caustic soda for the determination of phosphorus segregations in iron and steel. Jeffries has found sodium hydroxide a good electrolyte for the electrolytic etching of tungsten.

Relief Polishing.—The method of relief polishing for developing the structure depends for its success upon the difference in hardness which sometimes exists between the constituents of the alloy, and which produces a differential abrasion. The usual polishing on a hard rubber disc is followed by further polishing on a soft rubber backing. Only the very finest rouge or alumina should be used for this purpose. This method has been used by Osmond for annealed steel but is seldom used at present as the chemical method of etching is more satisfactory.

Polish Attack.—A very similar method of developing the structure is that of rubbing the section on parchment moistened with an etching reagent. This was called "polish attack" by Osmond who first used the method. He used an extract of licorice, or a 2 per cent. solution of ammonium nitrate, with precipitated calcium sulphate, to moisten the polishing cloth. Hudson, who highly recommends this method, uses ammonia for copper and its alloys, particularly the brasses. He describes the method as follows:

"The parchment is thoroughly moistened with water and then spread on a smooth wooden support. Three or four drops of dilute ammonia (1 part strong ammonia to 1 part water) are sprinkled on the parchment, together with a little freshly ignited magnesia made from carefully prepared and thoroughly washed magnesium carbonate. The specimen is then rubbed gently but steadily, usually with a circular motion,

on the parchment for a short time (15 seconds), washed thoroughly, dried quickly on an old clean linen, and examined. If necessary the operation is repeated. By varying the amounts of magnesia and ammonia, and the strength of the rubbing, the crystals can be darkened to different degrees or the structure may be seen quite unstained and thoroughly outlined."

Gwyer uses a dilute solution of caustic soda and ignited magnesia for developing the structure of the light aluminum alloys, for example the iron-aluminum eutectic.

Heat Tinting.—A metallic surface, polished in the usual manner and heated in the air forms an oxide which produces a series of interference or temper colors. The color assumed depends upon the thickness of the film formed, so that if two constituents are present it will be seen under the microscope, in general, that they may be distinguished from each other by the differential coloring produced. This method of developing the microstructure has the advantage that it does not develop relief in the surface, as etching does.

The surface of the specimen should always be very carefully cleaned prior to heating to the tinting temperature. Stead recommends cleaning with a 1 per cent. solution of picric acid and a linen cloth, followed by heating to about 150° C. and rubbing on a chamois skin. The specimen is placed in a sand bath on a wire gauze with the polished surface up. Heat is applied from beneath by a moderate flame. From time to time the specimen is quenched in mercury (if in water, the water must not be allowed to run on to, and wet the oxide surface), and examined under the microscope to establish the desired end point.

Stead uses this method for the determination of phosphorus enrichments in steel.[1] For this determination the specimen is heated on a bath of molten tin at 300° C. until it takes on a reddish-brown color. The phosphorus-rich portions, which oxidize more readily, may be recognized by their blue color.

Heat tinting may be used to distinguish the phosphide of iron from the carbide of iron in white cast iron as the free carbide colors deeper than the free phosphide. Cu_3P and Cu_4Sn or δ may be distinguished in bronze by this means as the phosphide colors a beautiful blue while the Cu_4Sn colors yellow.

[1] For this and other methods, see STEAD, "Metallographic Methods for the Detection of Phosphorus in Steel," Cleveland *Inst.* of Mining Engineers, December, 1914.

Stead has advocated heating in an atmosphere of ammonium sulphide, chlorine, bromine, etc., at a temperature high enough to prevent any condensation on the surface of the specimen. The specimen floats on molten tin or lead and a stream of air is directed on to it from a water bottle containing a weak solution of the etching reagent.[1]

Hot Etching.—The specimens are at times etched while at an elevated temperature for the purpose of developing the structure stable at that temperature. Molten calcium chloride and hydrochloric acid (gaseous) have been used to etch steel at a red heat. Hanemann raised an objection to this method of developing the structure pointing out that the surface ultimately examined would not be a section through the cyrstals but simply the surfaces of the crystals which would form while the steel was being held at the elevated temperature.[2]

<div align="center">TABLE OF ETCHING REAGENTS</div>

Iron and steel:

General..	HCl in ethyl alcohol.
	Picric acid.
Commercial work, 100X and under.................	HNO_3 in amyl alcohol.
Annealed steels..................................	Picric acid.
Quenched steels.................................	Kourbatoff—B.
	Conc. picric acid.
Tempered steels.................................	Kourbatoff—C or D.
Quenched or tempered steels......................	Kourbatoff—A.
	HCl in alcohol.
For Fe_3C.......................................	Sodium picrate.
	Sulphurous acid.
Fe_3C vs. Fe_3P....................................	Heat tinting.
For phosphorus segregations......................	Complex reagents of Stead, Rosenhain and Le Chatelier.
For sulphides—macroscopic.......................	Mercuric chloride.
	Silver bromide.
Steel shapes—macroscopic........................	Tincture of iodine.
Phosphorus in mild steel.........................	Copper ammonium chloride.
Slag in steel—macroscopic........................	HNO_3 in amyl alcohol.
Slag in steel—microscopic........................	Conc. nitric acid.
Special steels...................................	Electrolytic etching.
	Aqua regia.
	HNO_3 in amyl alcohol.
Copper and brass.................................	Basic copper ammonium chloride.
	Ammonium persulphate.
	Ammonia.
	$Cr_2O_3 + H_2O_2$—Miller's reagent.
	Polish attack with ammonia.
	Electrolytic etching.
For lead and oxides..............................	Nitric acid.

[1] Stead, *Journ.* Inst. Met., 1914, No. 1, p. 135.

[2] See *Intern. Journ. Met.*, 1912, Vol. 3, p. 176.

TABLE OF ETCHING REAGENTS (*Continued*)

Copper and bronze...............................	Acid ferric chloride.
	Ammonium persulphate.
	Ammonia.
	Nitric acid.
Cu_4Sn vs. Cu_3P..............................	Heat tinting.
Copper alloys....................................	Ammonium persulphate.
	Nitric acid.
	Ferric chloride.
	Electrolytic etching.
Zinc and zinc alloys.............................	Caustic soda or caustic potash.
	Nitric acid + chromic acid.
Lead, tin,and bearing metals....................	Nitric acid (+ chromic acid).
	Hydrochloric acid.
	Silver nitrate.
Aluminum and aluminum alloys....................	Hydrofluoric acid.
	Caustic soda or caustic potash.
Noble metals....................................	Aqua regia.

The Metallographic Microscope.—The passage of light through the compound microscope and the reproduction of the microscopic image is made clear by Fig. 29. Briefly stated, the object, in this case, is illuminated by transmitted light coming from below. The objective acting as a simple lens, magnifies the object a certain number of diameters and reproduces it, as a real image, in the plane of the ocular. The ocular in turn reproduces this image, magnified a certain number of times, as a virtual image, at a distance of ten inches from the eye which is the average reading distance. The total magnification secured is equal to the product of the magnifications of the objective and the ocular.[1]

The fundamental difference between the microscope shown in Fig. 29 and a microscope for the examination of opaque objects is in the method of illuminating the object. Opaque objects must be illuminated by light which is reflected on to the specimen by a reflector which is situated above the microscope stage. Two different kinds of illumination are recognized: oblique, which is used principally in the study of the surface features of the microsection, and vertical (more properly, "normal" illumination), which is used principally in the study of the structure of the specimen.

The methods of illuminating the microsection are shown in Fig. 30. The method shown at *a* is seldom used as only a narrow band is in sharp focus. The method shown at *b* is commonly used for oblique illumination. Here the section is

The magnification obtained by a compound microscope equal, for instance, to 100 diameters (written X100) means that a line on the object appears to be 100 times as long when viewed through the microscope.

placed normal to the axis of the microscope so that light projected, as at 1, from a bull's-eye condenser would be reflected outside the microscope and the area would appear dark. Light falling on a surface irregularity, as at 2, would be reflected up the microscope
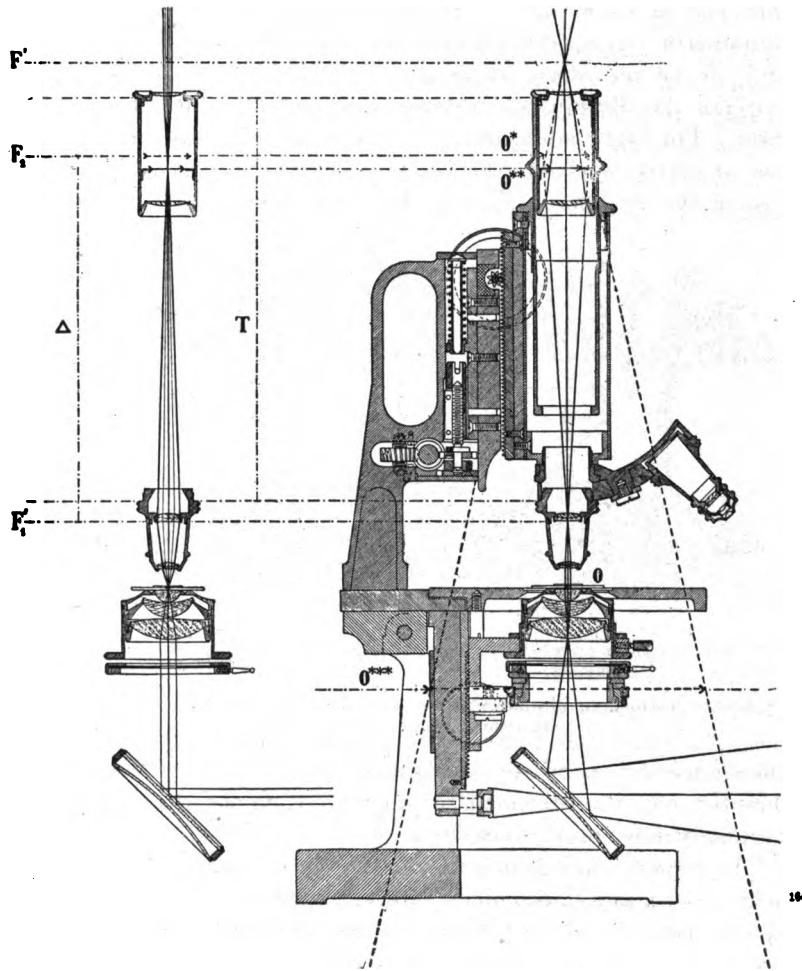
FIG. 29.—Path of the rays through the compound microscope. To the left —path of rays from a point object. To the right—path of the marginal rays. *T*, the mechanical tube length; Δ, the optical tube length. (*Carl Zeiss.*)

tube so that the area at 2 would appear bright. This method of illumination can be used, obviously, only in case there is sufficient room between the specimen and the objective. Other

illuminators designed to be placed in front of the objective are Sorby's parabolic reflector, in combination with a bull's-eye projector, the Lieberkuhn, which reflects light coming from below the stage down again on to the specimen, and the thin transparent mica slip, as shown at *c*. A very convenient form of the latter illuminator is placed on the market by Leitz and fits on to the end of the objective. Inasmuch as most of the light passes through the illuminator, a strong source of illumination must be used. For high power work, or where the working distance of the objective is short, the illuminator must be situated to the rear of the objective. The method most commonly employed is
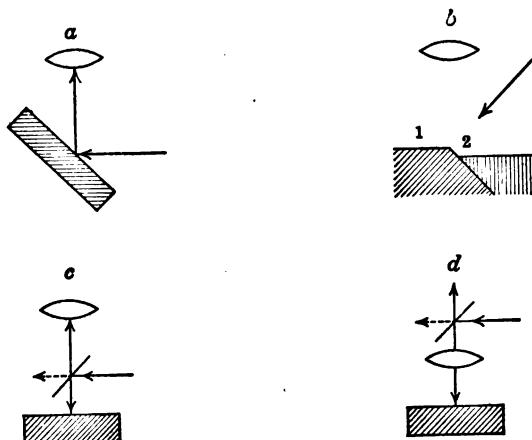
Fig. 30.—Methods of illuminating the microsection. The arrows indicate the direction and path of the light.

shown at *d*. A mirror, or other reflecting surface, is placed directly over the specimen so that the beam of light is reflected vertically down on to the section.

The large metallographical microscope, set up for both visual examination and photomicrography, consists of three parts—the optical bench, for furnishing the illumination, the microscope proper and the camera. These parts can be seen in Fig. 31 which shows the Martens-Zeiss metallographical microscope. For convenience, this microscope will serve as the basis for the following discussion. The principles involved are fundamental, and while certain details would necessarily be different for other types of microscopes, it would hardly be worth while here to consider so fully more than this one.

The optical bench consists of Nos. 1, 2, 3, 4 and 5 all mounted in common on a cast iron rail. No. 6 is the microscope mounted in common with the optical bench on a heavy stand. The camera is mounted on a separate stand and is connected to the microscope only when needed.

Illumination.—The source of illumination used in Fig. 31 is supposed to be an arc. In general, illuminants can be divided, for convenience sake, into two groups—those which are used to produce the so-called "critical illumination" in which the source of illumination is reproduced by the objective on the surface of the microsection, and those used in a projection system. Critical
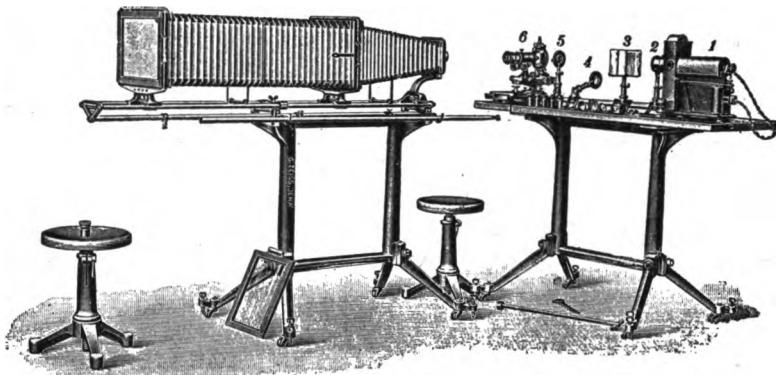
Fig. 31.—The Martens-Zeiss metallographic microscope with photomicrographic camera. (*Carl Zeiss.*)

illumination is designed principally for visual observation while the more complex projection system, devised at the Zeiss Works, is designed to give a stronger illumination, as is needed for photomicrography.

In critical illumination a disc of ground glass, or preferably of opal glass, at least one-half inch in diameter, is illuminated by a gas light, an incandescent globe or a Nernst lamp, or even by daylight. The illuminated disc is placed at a distance from the vertical illuminator which is equal to the distance from the latter to the lower focal plane of the eyepiece; *i.e.*, at such a distance that its image will be reproduced by the objective on the specimen. The most satisfactory illuminants for this purpose are Nernst's lamp and the 6-volt, concentrated filament Mazda lamp. The latter as supplied by Bausch and Lomb has been used very satisfactorily in the author's laboratory. It is exceptionally well

adapted to visual examination but is not powerful enough for photographic work.

For the purposes of photomicrography the principal illuminants which come under consideration are the calcium light and the arc light. The calcium light is very satisfactory as it produces a very pure white light and is exceptionally uniform. The light is made by heating a lime or magnesia disc with an oxyhydrogen flame which is concentrated to a small cone by the burner. In this way it can be made to approximate very closely the ideal "point of illumination." The great steadiness and uniformity of the calcium light makes it exceptionally useful in photomicrography.

The arc light is much more widely used in metallic microscopy as it is more powerful and is also more convenient to use   For most purposes the 5-ampere arc, either automatic or hand regulating, is sufficient. The exposures required are appreciably shorter than for the calcium light. If the microscope is unavoidably situated where the vibration is excessive, the 30-ampere arc is used so that exposures can be cut down to a fraction of a second. Direct current should be used with the arc light wherever possible, with the positive carbon in the optical axis of the illuminating system. The negative carbon, which should be somewhat smaller than the positive, is usually placed at an angle of 90°.[1]

Mercury vapor lamps have also been tried, but the advantage of using (monochromatic) light from this source is more than overcome by the inability to construct the lamp in a compact form.

The arrangement of the optical bench as used with the Martens-Zeiss microscope is shown in Fig. 32. The source of light (1) is placed at the focal point of the collecting lens (2) which here acts as a collimator. The beam of light leaves (2) as a parallel bundle of rays and is converged by (3) and brought to a focus in the plane of the small iris diaphragm (5), the distance between (3) and (5) being about six inches. This set up should be tested by opening the diaphragm (4) and closing down the diaphragm (5); when, if the lens (2) is properly adjusted an image of the luminous crater can be seen on the window of the iris diaphragm (5). The illumination at (5) will not be as intense as at (1) on

---

[1] Relative intensities of illumination for different sources of illumination are as follows: the sun, 800; D. C. arc, 130; A. C. arc, 70; calcium light, 10; Nernst lamp, 3.0; carbon filament, 0.8; acetylene lamp, 0.07.

account of the fact that a certain amount of light is lost, principally in passing through the lenses.[1] The large iris diaphragm (4), the image of which is brought to a sharp focus on the surface of the specimen, is introduced to eliminate stray and unnecessary rays from the outer portions of the lens, or to cut down the field of illumination. This is best accomplished by first focusing the corner of a piece of thin paper, held on the lens (3), on the specimen by moving lens (3) laterally along the optical bench. The diaphragm (4) is thereupon placed as close as possible to (3). By varying the opening of this diaphragm the size of the field of illumination is regulated. A tank of water with parallel sides is at times placed on the optical bench between (2) and (3) to absorb the heat rays. This may be seen at (3) in Fig. 31.
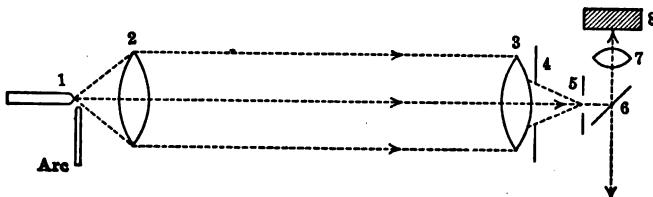
Fig. 32.—Scheme of illuminating the microsection.

Vertical Illumination.—The vertical illuminator is placed on the inside of the microscope tube directly over the objective. This arrangement for the two principal types of illuminators, the plane glass and the totally reflecting prism, is shown in Fig. 33, *a* and *b*, and again in Fig. 34. The function of the plane glass illuminator (*a*) is as follows: The source of light is assumed to be a point of light inside the diaphragm (1) which corresponds to diaphragm 4 of Fig. 32. The light passes through the small diaphragm (2) and on to the vertical illuminator (3) which is inclined at an angle of 45° to the beam of light (also to the optical axis of the microscope). About 75 per cent. of the light from (1) passes through the plane glass and falls on to the wall of the

[1] No advantage is gained ultimately by increasing the diameter of the lenses (3) and (2) in order to collect more of the rays from (1). With a given focal distance, the amount of light collected will increase as the diameter of (2) but on the other hand, the thickness of the lens will also increase. This effect is doubled, as the thickness of the lens (3) will also be increased. The loss due to absorption is greater than the gain by using lenses of greater diameter. The present tendency in the design is to make the lenses (2) and (3) as thin as possible, in order to cut down the absorption.

microscope. The rest, however, is reflected vertically downward and brought to a focus on the specimen (5) by the objective (4), which here acts as a condensing lens. What is true for the middle
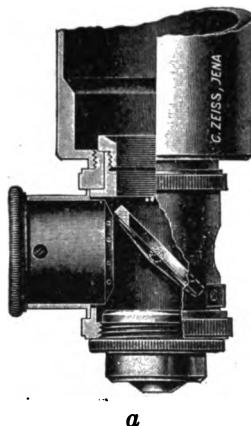
a

FIG. 33a.—Plane glass illuminator.
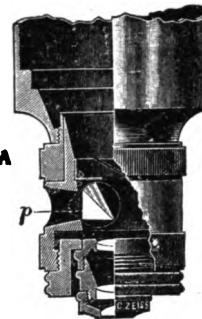
b

FIG. 33b.—Prism illuminator.
(*Carl Zeiss.*)

point of the diaphragm (1) is also true for the entire surface, so that an image of the diaphragm (1) is reproduced on the surface
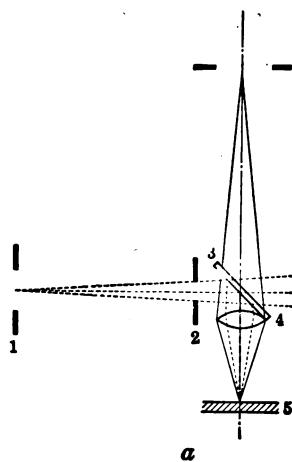
a
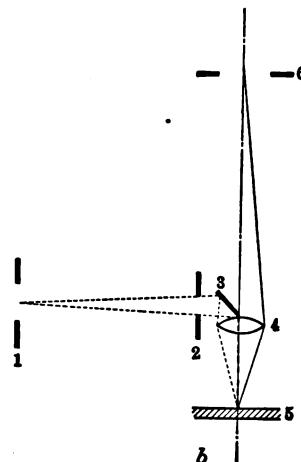
b

FIG. 34.—Diagrammatic representation of vertical illumination; at *a* with the plane glass and at *b* with a prism. (*Carl Zeiss.*)

of the specimen (5). In other words, a shadow of the diaphragm (1), in sharp focus, is cast upon the surface of the specimen. Alf of the points situated within this image, the so-called "field of

illumination," reflect light back through the objective, a part of which reaches the eye as shown by the solid lines. That part of the specimen which is visible to the eye is called the "field of vision." The diaphragm (1) should be closed down so that the field of illumination is but slightly larger than the field of vision, in order to cut out as many of the stray rays as possible, which otherwise would cause haziness. The diaphragm and vertical illuminator are adjustable so that the field of illumination can be made concentric with the field of vision. The diaphragm (2) regulates the size of the pencil of light and, therefore, the intensity of the illumination. This is varied according to the nature of the specimen. As the diaphragm (2) is stopped down the aperture of the illuminating pencil decreases and therefore the focal depth of penetration increases. This acts at first to improve the definition and contrast, but, on the other hand, the illumination diminishes as the square of the diameter of the opening, and, beyond a certain point diffraction fringes become pronounced and the resolving power diminishes. The diaphragm (2) has no effect on the size of the field of vision.

The arrangement using the totally reflecting prism is shown at (b). The functions of the two diaphragms (1) and (2) remain the same. (3) is a totally reflecting prism or mirror which reflects all the light falling on it vertically downward. As it occupies one-half of the cross section of the microscope tube (more or less), the size of the beam of light from (1) can be increased to one-half the opening of the objective as a maximum. The light coming from (5) can also make use of only one-half of the aperture of the objective, as all the light falling on the illuminator (3), on the return, passes out of the microscope through the diaphragm (2) and is lost. The totally reflecting prism causes a geometrical division of the beam of light as one-half the entire beam is reflected outside the microscope. The plane glass illuminator, on the other hand, splits up each individual ray so that part of it reaches the eye and part of it is deflected outside the microscope; but geometrically the beam of light remains unchanged. A further effect of the totally reflecting prism is that light falling on the surface (5) is not vertical, as in (a) but is slightly inclined.

The specific intensity of the illumination given by the prism illuminator is comparatively high as a solid bundle of rays is projected down on to the specimen and up to the eye. The same is not true of the plane glass type as a considerable portion of

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each ray is lost in its course, although the bundle, as a whole, remains intact. Due to this latter fact the resolving power of the plane glass illuminator, which depends on the size of the aplanatic cone, is very high, much higher than with the prism illuminator, whose position in the microscope tube cuts down the effective aperture, and therefore the N.A.[1]

Each illuminator possesses its own individual advantages so that a choice must be made to suit the conditions. For low to medium magnifications the totally reflecting prism is generally used. It gives brighter reproductions, requires less time for exposure in photomicrography and produces good results optically. The plane glass illuminator is used for high magnifications, when its greater resolving power is especially desirable.[2]

Other illuminators are used for this work but, inasmuch as they do not differ in principle from the two types described, they will not be considered in detail. This does not include the parabolic and other external illuminators which have been superseded by the vertical types.

The Stage.—In routine examinations the specimen is mounted in plasticene on a glass slide or other holder. To level the surface, a brass ring with parallel ends, or similar arrangement, is passed over the specimen, and its surface is forced into the plane of the brass ring by means of a glass slide. When the slide is mounted on the microscope stage, the surface will then be normal, or approximately normal, to the optical axis. For more accurate work, the slide should be mounted on a secondary stage which is provided with leveling screws to allow tilting the specimen in two directions at right angles to each other. The specimen is first brought to within one millimeter of one of the low-powered objectives, preferably the 16 mm. objective. The mechanical stage is tilted by means of the two leveling screws so that the prepared surface appears parallel to the front glass of the objective, when viewed vertically and horizontally. A piece of paper held back of the lens furnishes a background by means of which this adjustment can be very accurately carried out. A still finer adjustment can be made for photomicrography by observing the specimen through the microscope with a high-

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[1] It should be noted that the prism illuminator, even though it is in the path of the rays, is not to be seen.

[2] For the advantages secured by using the plane glass illuminator, see BENEDICKS, *Met.*, 1909, Vol. 6, p. 370.

powered objective and noting the direction of the displacement necessary, first horizontally and then vertically, to bring the entire field of vision into sharp focus. This adjustment is made first with one of the leveling screws and then with the other.[1]

Mechanical stages are used, quite extensively, so that the specimen can be more conveniently shifted during observation and also to facilitate relocating the same part of the specimen in later work.

Lenses.—The lens system of the compound microscope consists of the objective and the ocular. Of these, the more important is the objective whose function is to resolve the details of the structure and project the magnified image to the plane of the ocular. Its most important properties are the equivalent focal distance, which gives the magnifying power, the numerical aperture (N.A.), which gives the resolving power, the size of the field and the working distance, as well as the optical correction.

The magnification of the objective, or the "initial magnification," is given by Zeiss as 250 mm., the normal reading distance, divided by the equivalent focal distance. The 16 mm. objective magnifies about sixteen times and other objectives in inverse ratio to their equivalent focal distances. Other firms have different means of expressing the initial magnifications of their objectives; thus, the initial magnification of a Leitz 16 mm. apochromat is given as 11.5.[2]

The resolving power, which is the ability of the lens to make visible the fine details of a structure, is given by the N.A. of the objective, which is equal to the sine of one-half the angle of aperture multiplied by the refractive index of the medium between the specimen and the front lens of the objective: $N.A. = a \sin \alpha/2$. This shows that the resolving power depends on the

[1] Dr. Rosenhain has described a leveling device for metallographic specimens, using the principle known as "auto-collimation." By means of this optical device the upper surface of the specimen can be brought very accurately to a position which is normal to the optical axis, or, what is at times very advantageous, to a position which will allow for any inaccuracy in the adjustment of the microscope stage. (It should be noted that the leveling stage described above allows the same correction to be made.) See *Journ. Inst. Met.*, 1915, Vol. 13, p. 160.

[2] It should be noted, in this connection, that the equivalent focal distance of the objective is frequently different from that given by the maker; for example, the initial magnification of a 4 mm. objective will not necessarily be four times that of a 16 mm. objective.

size of the cone of light collected by the lens from each point on the specimen. Further, we have as the smallest size which can be resolved: $\delta = \dfrac{\lambda}{N.A.}$,[1] where λ equals the wave length of the light used. This function shows, not only the capacity of the objective but it demonstrates the value of using light of a short wave length to resolve fine structures.[2]

The high-powered objectives are so constructed that a liquid of high refractive index can be used between the object and the front glass of the objective. The liquids commonly used are water ($R.I. = 1.3$) and oil of cedar wood ($R.I. = 1.52$). In this way numerical apertures exceeding unity can be secured.

There are certain defects, inherent in all optical systems, which must be overcome or "corrected," and the value of the objective depends largely on the extent to which the correction is made. These defects are known as spherical and chromatic aberration.

Spherical aberration arises from the fact that the rays passing through the outer edge of the lens (the marginal rays) and rays passing through near the center do not come to a focus at the same point along the optical axis. This defect reduces the effective aperture or the size of the cone of light which the lens is capable of bringing to sharp focus—the "aplanatic cone"—and the outer edges of the image appear blurred and tinged with color even though the central part is in sharp focus.

Chromatic aberration arises from the fact that a lens acts as a prism and disperses the light passing through, so that light

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[1] This is for normal illumination. For oblique illumination: $\delta = \dfrac{\lambda}{2\,N.A.}$

[2] The following table is reproduced to show the relation between the resolving power and the numerical aperture and the wave length of the light used. *Journ.* Royal Microscopical Society.

N.A.	R.P. as the maximum number of lines per inch which the objective renders as separate lines	
	White, $\lambda = 0.5269\ \mu$	Blue, $\lambda = 0.4861\ \mu$
1.40	135,000	146,000
1.30	125,000	136,000
1.00	96,000	105,000
0.50	48,000	52,000

of different colors (wave lengths) comes to focus at different distances along the optical axis and the various images do not coincide. Further, the images of the different colors are not of the same size so that color fringes are formed, as in the spectrum.

We shall now consider the two leading types of objectives, the achromatic and the apochromatic, bearing in mind the above points. They are differentiated by the extent to which the corrections for spherical and chromatic aberration have been carried out.[1]

In the achromatic objectives light of only one wave length, the brightest color to the eye, passes through without producing spherical aberration. This means that perfectly sharp images are secured with only one color and that other images are blurred so as to form color fringes and to cast a general haze over the entire field. This is lack of complete correction and is due to the "chromatic difference of spherical aberration." The apochromatic objectives, on the other hand, produce images which are nearly equally distinct for all colors so that the quality of the image is independent of the light used for illumination. Furthermore, the color correction in achromatic objectives is adequate only in one zone and the definition falls off toward the eenter and the margin, while in the apochromatic objectives the color correction is uniform over the entire field. Chromatic aberration in achromatic objectives is corrected for two colors— red and violet—by using appropriate combinations of optical glass and lenses. This leaves a "secondary spectrum" of apple green which limits the aperture which can be employed. However this correction is perfect only within the limited zone. The apochromatic objectives produce coincident images with three different colors and this is true for the entire field, so that the various images, besides being individually perfected, are brought more nearly coincident in the same focal plane to produce uniform and sharply defined images. For these reasons the

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[1] Prior to 1886 the achromatic objectives were in general use as the most satisfactory objectives. In that year Abbé introduced the present apochromatic objectives, the production of which depended very largely on the efforts of Schott and Gen. Jena, who produced a new type of optical glass. See ABBÉ, "Gesamelte Abhandlungen," Vol. I. The general principles underlying the construction and use of the microscope are given in SCHEFFER, "Wirkungsweise und Gebrauch des Mikroskopes."

apochromatic objectives combine, very satisfactorily, a high resolving power, superior definition and a wide range of magnification and this is true whether the illumination is vertical or oblique or with colored or with white light.

The correction of the spherical aberration improves the flatness of the field, but the greater numerical aperture secured works in the opposite direction so that lack of flatness of the field is now considered an unavoidable characteristic of the more highly corrected lenses. It must be borne in mind that the correction for spherical aberration is effective only if the tube length, for which the objective is made, is actually employed.[1]
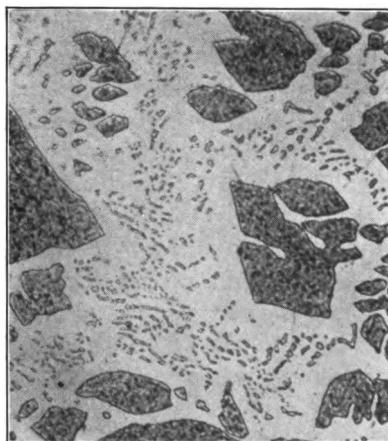
Fig. 35.—Secondary eutectoid in a copper-tin-zinc alloy. (× 1250.)

The superior correction and high resolving power of the apochromatic objectives is at once apparent from the clear, well-defined images produced and the ease with which even the minute details of the structure are brought out. This is of particular importance in photomicrography where pleasing reproductions which leave no doubt as to the nature of the structure which it is sought to reproduce, are both desirable and necessary. In this connection the author ventures to reproduce a photograph at 1250 diameters which he took with a Zeiss 2 mm. apochromat, N.A. 1.40—See Fig. 35. Blue light was used for illumination and it may be noted that the image shows adequate

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[1] That is, the correction for spherical aberration holds strictly only if the "sine relationship" is observed.
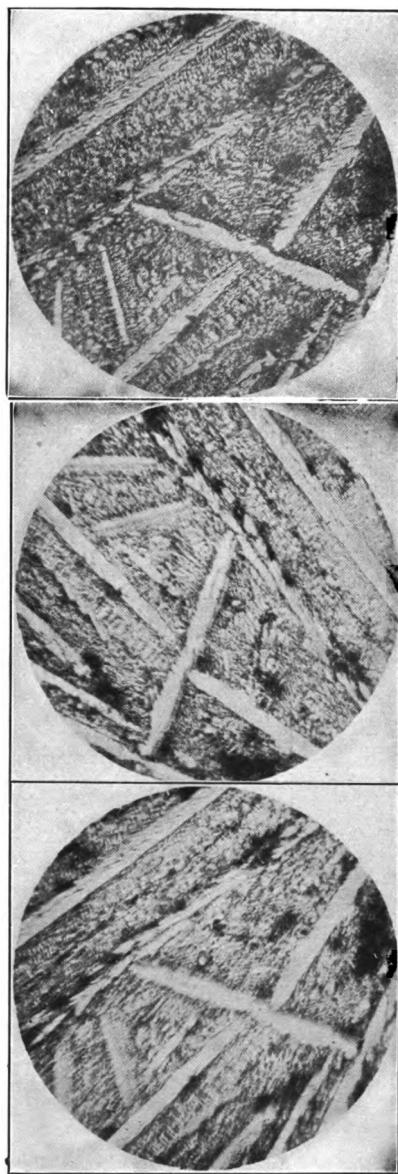
Fig. 36.—To show the effect of different colored light with an achromatic objective: *a*, white, *b*, blue, and *c*, yellow. Photographed at × 100, reduced to × 60.

correction for spherical abberation, while the short wave length
of blue light assisted materially to bring out the fine details.

The use of achromatic objectives in photography restricts
the illumination to yellow light, the only color which is sub-
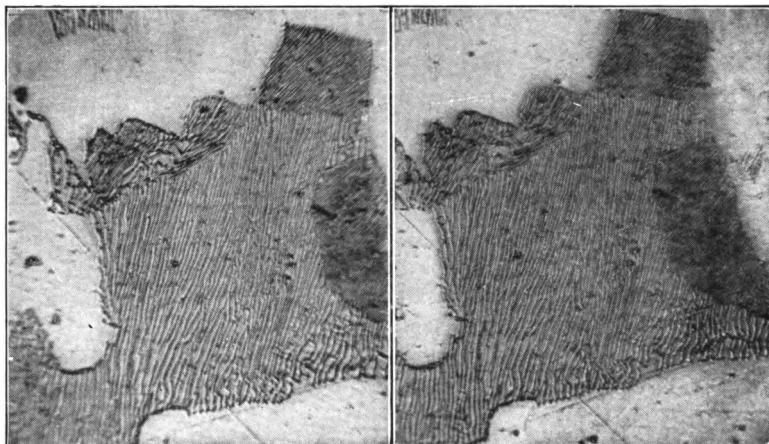
FIG. 37.   × 800.   FIG. 38.   × 800.
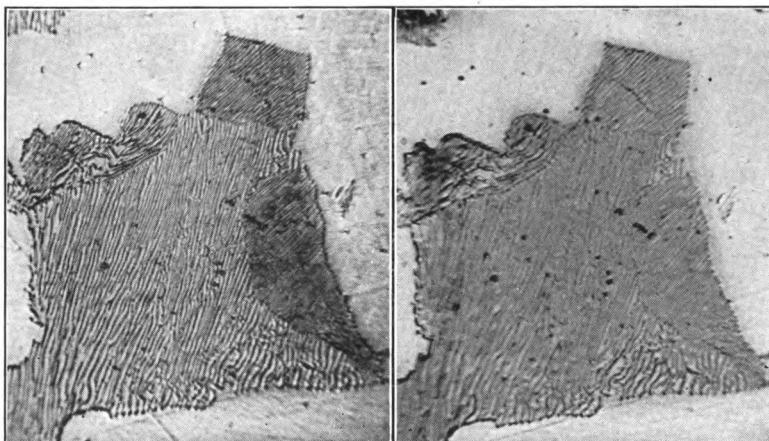
FIG. 39.   × 800.   FIG. 40.   × 800.
To show the effect of different colored light with an apochromatic objective.
FIG. 37, white.   FIG. 38, blue.   FIG. 39, yellow, plane glass illuminator.
FIG. 40, yellow, prism illuminator.

ject to spherical aberration. When white light is used, the
so-called visual and chemical images do not coincide (chromatic
aberration) while if blue light is used, the image is not sharply

defined (spherical aberration). Fig. 36, a and b illustrate the effect of white and blue light when used with an achromatic objective. The use of monochromatic yellow light largely eliminates these defects, as can be seen from Fig. 36c which shows the same subject as a and b, photographed with a yellow filter. A similar study made with a 2 mm. apochromatic objective (oil immersion) is shown in Figs. 37, 38 and 39. A comparison of these photographs shows that the quality of the reproductions is much less dependent on the kind of light used. Fig. 40 is added to bring out the effect of the totally reflecting prism in reducing the resolving power.

Apochromatic objectives are named according to their equivalent focal distances as given in Table 3. The size of the field viewed in the objective is given in the last column. With higher powered oculars, this decreases in direct ratio to the increase in magnification, but, however, is not affected by the numerical aperture.

TABLE 3.—APOCHROMATIC OBJECTIVES (ZEISS)

Equivalent focal distance	Numerical aperture	Initial magnification	Working distance, (a) mm.	Diameter of field, (a) mm.
16 mm. dry..........	0.30	15.5	5.0	2.00
8 mm. dry..........	0.65	31	1.0	1.00
4 mm. dry..........	0.95	63	0.2	0.45
3 mm. dry..........	0.95	83	0.15	0.35
3 mm. oil immersion.	1.30	83	0.20	0.35
3 mm. oil immersion.	1.40	83	0.16	0.35
2 mm. oil immersion.	1.30	125	0.16	0.25
2 mm. oil immersion.	1.40	125	0.12	0.25

(a) When used with compensating eyepiece No. 4 with a tube length of 160 mm.

The achromatic objectives are named arbitrarily and the catalog of the maker should be consulted for their constants. The ordinary objective is corrected for use with covered objects so the lenses used with opaque objects (uncovered) must be corrected for use without a cover glass. At the same time they are constructed with short mounts to allow the illuminator to come as close as possible to the back lens.

The oculars used with the achromatic objectives are ordinary oculars, usually the Huyghenian. They are named arbitrarily and here again the catalog should be consulted for magnifications,

etc. If these were used with the apochromats, color fringes would be produced on the outer edges due to the various colored images being of different size and their consequent overlapping. On this account compensating eyepieces, over-corrected in the opposite sense, are used with apochromatic objectives. They are known as "compensating oculars," and are named according to their magnifications.

The oculars used have magnifications ranging from 2, used for examining a large field, to about 24 diameters. Generally an ocular magnifying 12 times is sufficient to bring out the details of the image. Higher powers add nothing to the image but merely increase the size of the parts and decrease the size of the field. Barnard states that a total magnification of 750–800 diameters is sufficient for an experienced observer to see all there is in the image, even when the best lenses are used.

Photomicrography.—If a permanent record of the microstructure is desired, the microscopical image is either drawn free hand or reproduced photographically. The quality of the micrographs which have issued from the laboratory of Professor Arnold are admirable examples of the results which can be secured by the former method, but the photographic method has proven to be more practical and is the one generally used. For this purpose the regular ocular is replaced by a projection ocular, and a camera of variable bellows length is brought into position to make a light tight connection with the microscope. The projection ocular reproduces the image on the ground glass plate or the photographic plate, as the case may be, at the rear of the camera. To secure good reproductions it is necessary to have the entire system in adjustment, which can be obtained only by observing the points discussed above, particularly those for illumination. The technique of photographing metals is very similar to that required for other purposes so a detailed description will not be necessary.[1]

The magnification of the image should be determined by means of a stage micrometer, usually ruled in hundredths of a millimeter, whose image is projected on to the focusing screen. The magnification can be readily determined from the distance between the rulings. Magnifications determined from the equivalent focal distance of the lens, as given by the maker, cannot be relied upon.

[1] For greater details, see BARNARD, "Practical Photomicrography," 1911.

The projection oculars used vary in magnifying power from about 2X to 4X and are constructed so that the distance beween the front and rear lenses can be varied to correspond to the bellows length. The correct setting, which focuses the image on the photographic plate without introducing spherical aberration, is determined by means of a scale which should read to correspond to the bellows length.[1]

The selection of the lenses and bellows length is very important and it may be well to state a few general rules regarding this point. The idea in selecting the objective to give any desired magnification, is to use one with as high an initial magnifying power as possible in order to take advantage of the superior resolving power. By the same token, the bellows length is to be shortened as far as is practical. The use of the short bellows length requires the higher power projection ocular (Zeiss No. 4 as compared to No. 2); otherwise the field will not be sufficiently flat.

The following table, after Hanemann, gives satisfactory combinations for certain standard magnifications.

TABLE OF MAGNIFICATIONS

Magnification	Objective	Projection ocular	Bellows length, cm.
100X	Achromat A	.....	125
150X	Apochromat 16 mm.	No. 4	50
300X	Apochromat 8 mm.	No. 4	50
500X	Apochromat 4 mm.	No. 4	50
700X	Apochromat 3 mm.	No. 4	50
1000X	Apochromat 2 mm.	No. 4	50
1200X	Apochromat 2 mm.	No. 4	60

Magnifications of less than 100 diameters are secured with micro-planars or micro-tessars of greater focal lengths. These lenses are adapted for use with either the microscope or the camera.

Color Screens.—It is usually found to be desirable to photograph sections in colored light of some kind. The principal reason for this with colored subjects is to increase the contrast between different parts of the specimen. Many times two different

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[1] The use of ordinary oculars, whose eye lenses are not variable, requires the adjustment of raising the microscope tube to focus the image. This method is not satisfactory in the finer work as it introduces a change in the optical tube length of the microscope.

colors which present considerable contrast to the eye will, on account of their relative actinic values, produce images on the photographic plate with very little contrast. A general rule to follow is to photograph two colors in light which comes intermediate between them, in order to increase the contrast. If the two colors come together in the spectrum, light should be used which is removed from the two as far as possible (Barnard).

Another valuable function performed by monochromatic light, especially if it be of short wave length, is to increase the resolving power. Many very fine-grained structures appear with greater detail when photographed with blue light.

It will be remembered that achromatic objectives are so corrected that the visual and chemical images do not coincide. This defect can be overcome by photographing with monochromatic yellow light, which produces images free from aberration and therefore with good definition. Apochromatic objectives suffer less from optical defects so that it makes little difference here whether white, blue, yellow or green light is used.

Some very efficient light filters are made by Wratten and Wainwright (Eastman Kodak Company). They absorb practically all of the light except that which is intended to pass, and work well with stronger illuminants. Some very instructive booklets on light filters are issued by the company and should be obtained by those interested in the subject.

Fluid light filters can also be made from salt solutions placed in glass cells on the optical bench. Yellow filters, for use with the achromatic objectives, can be made from saturated solutions of either picric acid or potassium bichromate in distilled water. Zettnow's green filter is made by dissolving 160 grams of pure copper nitrate and 14 grams of pure chromic acid in 250 cc. of water. This solution absorbs both the blue and the red ends of the spectrum, but by varying the relative amounts of the salts the absorption can be varied until the correct light transmission is secured, as determined by a spectroscope. A blue filter can be made by dissolving 10 grams of copper sulphate in 45 grams of ammonia (0.96).

Plates.—The plates used should be fine-grained and what are known as "slow" or "medium" speed. It should be borne in mind that the ordinary dry plate is much more sensitive to blue light than to either green or yellow. "Isochromatic"

plates are made sensitive to yellow as well as to blue and are to be preferred to the ordinary plate except for certain purposes. Of this grade, Seed's L-Ortho and Cramer's Iso have given excellent results and in metallographic work are more useful than the panchromatic plates. More recently plates have been made which are sensitive to all the colors of the spectrum, viz., the "panchromatic" plates. These are the Wratten and Wainwright M, the Seed's Process Panchromatic, and the Cramer Spectrum plates. It is always better to use "backed" plates to prevent the halation which is produced by light reflected from the back surface of the plate. Other useful plates are the Seed's Process plates, and the Cramer Contrast plates, which are sensitive to the blue and violet rays.

The time of exposure, which depends upon the intensity and character of the light, the speed of the plate and the magnification, varies from a fraction of a second with the 30-ampere arc to several minutes with weaker illuminants and colored light. This time can be determined in advance in various ways, such as by exposing successive portions of the plate for times which increase in geometric ratio; but it can usually be estimated closely enough by an experienced worker to come within the latitude of the plate which should be about 2.

A general rule to follow here is to expose for the darker parts of the image to make certain that they will be recorded. The developing should be done with particular reference to the high lights. It is generally necessary to increase the contrast between the different parts of the image so the conditions should be chosen to increase, rather than decrease, the contrast. After sufficient contrast has been secured to give pleasing reproductions, attention should be directed toward rendering the details as clearly as possible.

A useful developer for the usual plates, and one which is used almost exclusively in the author's laboratory, is ferrous-oxalate, which is prepared as follows:

Solution A		Solution B	
H_2O............	100 c.c.	H_2O............	400 c.c.
$FeSO_4$..........	30 grams	Potass. oxalate..	80 grams

Add 1 part of A to 4 parts of B and mix immediately, 50 c.c. in all.

Fresh solution should be used for each plate. There are numerous other developers which may be used to bring out contrast and,

detail and their formulæ may be obtained from the makers of the plates.

The time of development is usually from five to twenty minutes and is continued until the image comes through strongly on the reverse side of the plate. Another method of estimating the correct time is to multiply the length of time which elapses until the image first appears, by a certain factor, to obtain the total time. The ordinary procedure is to develop in a low red light but the panchromatic plates, being sensitive to red, must be developed in a green safety light or else in total darkness for a predetermined length of time. If the plate is known to be over-exposed, a few drops of a solution of 10 grams of KBr in 100 c.c. water (a restrainer) are added to the developer, while if the plate has been under-exposed a few drops of a solution of 10 grams Na_2-CO_3 in 100 c.c. water are added.

After developing, the negative should be rinsed off in water and placed in a fixing bath composed approximately as follows:

$$\text{Water} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad 1000 \text{ c.c.}$$
$$\text{Hypo} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad 250 \text{ grams}$$
$$Na_2SO_3 \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad 25 \text{ grams}$$

The plate is allowed to remain in this solution for at least a few minutes after the yellow film has all been dissolved. After this, the plate is placed in running water for one hour and placed on a drying rack to dry. In the summer time it is well to harden the coating by placing the plate in a saturated alum solution for ten minutes.

Under-exposed negatives are usually of no account. Over-exposed negatives contain sufficient detail but are thin and lacking in contrast. They may be intensified by treatment with a saturated solution of bichloride of mercury, containing 0.5 per cent. HCl, until bleached through to the back. The negative is then placed in a ferrous oxalate solution, made of one part of a saturated ferrous sulphate solution added to six parts of a saturated potassium oxalate solution. The plate remains in this solution until thoroughly black. An alkaline developer or even weak ammonia may be used to darken the plate.

In laboratories where photomicrographs are kept on file, a record should be made of the illuminator, light filter, objective, projection ocular, adjustments of the iris diaphragms, bellows length, magnification, time of exposure, as well as details of the

preparation of the microsection. A beginner should always keep accurate account of the above factors, at least until he understands their effects in photomicrography.

A print is obtained from the negative, in the regular way, by means of printing-out paper or developing paper (gas light paper). If a dark room is available, a good developing-out paper is the handiest for this purpose, using either gas light or electric light for illumination. The paper used should give both contrast and detail, such as Cyko paper, Azo F Hard X, or Regular Velox, all of which should have a glossy finish to give detail. Instructions for developing these papers accompany the package, but metol-quinol developer may be used, with either hypo or chromium fixing bath.

Either the gelatine or the celloidine daylight papers are satisfactory, if no dark room is available, but a grade to give contrast and detail should be selected. Directions as well as recipes for toning and fixing baths, always accompany the paper.

By drying the prints on a squeegee board, which has been cleaned with alcohol and coated with a thin layer of talcum powder, a brilliant surface is obtained which is very effective and pleasing.

MICROSCOPES AND ACCESSORIES.

Desk Microscopes.—Most of the manufacturers of the large instruments (to be discussed later) also make microscopes of a smaller type which will be referred to here as Desk Microscopes. These microscopes serve a very useful purpose in that

FIG. 41.—Campbell-Leitz microscope. (*E. Leitz.*)

they afford means for a hasty or preliminary examination under the lower magnifications, in less time than is usually required by the larger microscopes. They are also useful for following the etching process. If desired, a small camera will be supplied with the microscope for obtaining photomicrographs.

A useful microscope of this type, in that daylight is used for

illumination, is the Campbell-Leitz microscope. This apparatus, in the form shown in Fig. 41, has given very satisfactory service, although it is only fair to say that there is little to choose between the various microscopes of this type, except the lenses and the means of securing the illumination. The method of illumination used in the Campbell-Leitz microscope, will be regarded in this respect as a distinct advantage.

The Martens-Zeiss Microscope.—Carl Zeiss, Jena, manufactures a large microscope designed by Martens, especially to meet the requirements of metallography. The tube always re-
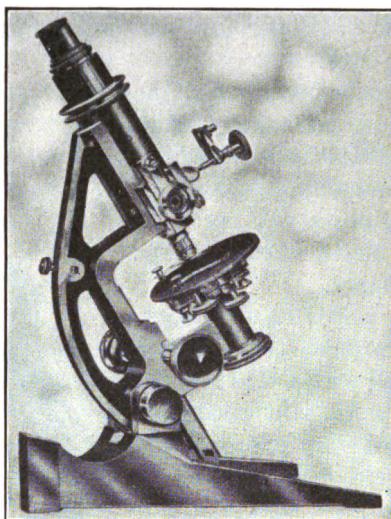
FIG. 42.—Rosenhain microscope. (*R. and J. Beck.*)

mains in a horizontal position and both coarse and fine focusing are done with the stage, allowing the tube to remain adjusted to the optical axis of the illuminating system. Photomicrographs at low magnifications can be secured by unscrewing the two end caps of the microscope tube and inserting an auxiliary tube holding the micro-planar which projects the image directly on to the photographic plate.

The stative 1-S of Zeiss has also been successfully used as a metallographic microscope as it can be used in both horizontal and vertical positions. This stand is exceptionally well constructed and certainly stands in the first rank of microscope stands which are used in metallic microscopy.

Watson & Sons' Horizontal Microscope.—A microscope similar in construction to the Martens-Zeiss is made by Watson & Sons, London, and will not be described in detail.

Rosenhain Microscope.—A large and well-designed microscope for use in works practice and in scientific laboratories alike, is made by R. & J. Beck, London, according to Rosenhain, as shown in Fig. 42. It is very solidly built, giving great stability while in either a horizontal or a vertical position. The construction
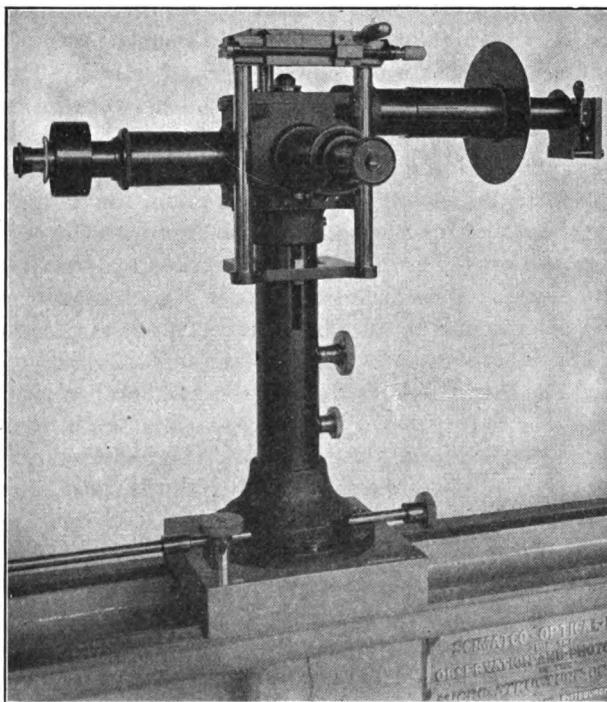
FIG. 43.—Metallographical microscope of the inverted type. (*Scientific Materials Company.*)

of this microscope makes it especially suited to the microscopical examination of metals under strain, due chiefly to the mechanical stage, which permits a complete revolution, and to the illuminating system, which is specially designed for oblique illumination.[1] While the choice of a microscope depends considerably upon the individual, still it may be said of the Rosenhain microscope that

[1] For a more complete description of this microscope, see ROSENHAIN, *Journ.* Royal Microscopical Society, 1906, p. 146.

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it offers all that can be desired of a metallographical microscope of the direct type and considerably more than other stands not designed particularly for the purpose.

Le Chatelier Microscope.—A metallographical microscope was designed by Le Chatelier especially to meet the requirements of metallic microscopy. This is shown in Fig. 43. The optical bench, the microscope stand and the camera are all mounted in common on a large cast iron bench. The distinctive feature of this design is the "inverted" stage. By simply placing the microsection on the stage, with the prepared surface down, the field is brought into a position normal to the optical axis. This is to be regarded as a special advantage in routine work on account of its simplicity and time saving. The vertical illuminator is of the prism type, and possesses all the disadvantages of this type of illuminator. By means of a rotating prism the image can be directed either on to the photographic plate or into the ocular for visual observation. The lenses generally used are the Zeiss apochromatic objectives corrected for a tube length of 250 mm.[1]

Another microscope of the Le Chatelier type, as designed by Guertler and modified somewhat by Campbell, is made by Leitz, Wetzlar. The Leitz Micro-Metallograph differs from the Le Chatelier model in that the optical system (iris diaphragms, vertical illuminator, etc.) can be adjusted to suit any combination of lenses. It is possible thereby to remove the haziness of the field due to the partial reflection on the surfaces of the lenses. In this instrument the plane glass and prism illuminators are interchangeable. This microscope is well adapted to works practice on account of the ease of mounting specimens and obtaining suitable photomicrographs.

The illuminator used with this microscope is rather different from the ones used with other stands and has been described by Guertler.[2] A small side tube is placed at the window of the illuminator and in the optical axis of the illuminating beam. This tube contains a small condensing lens which can be shifted laterally, with reference to the illuminator. The distance between the lens and the illuminator should be greater for high powers than for low powers, to secure the maximum efficiency of the system. A small iris diaphragm is placed in the tube to

[1] The Le Chatelier microscope is made in this country by the Scientific Materials Co.

[2] *Met.*, 1909, Vol. 6, p. 651.

regulate the size of the field of illumination. The illuminating beam from the arc lamp is focused at the outer end of the small tube.

Reichert Microscope.—Another modification of the Le Chatelier microscope is made by Reichert, Vienna. Two of its chief features are the special vertical illuminator, which is a combination of the totally reflecting prism and the plane glass illuminator, and the reflecting camera, which facilitates focusing the image. This microscope finds the same commercial application as the Le Chatelier and the Guertler-Leitz.

Bausch & Lomb Microscopes.—Bausch & Lomb are now constructing metallographical microscopes of both the direct and inverted types. The latter microscope is very similar to the Guertler-Leitz. A concentrated filament Mazda lamp or a small arc lamp may be used interchangeably in the lamp housing, with their adjustable aspheric condensing lenses. At present, only the achromatic objectives are supplied with these microscopes.

Holz Microscope.—A microscope of the inverted type has just recently been put on the market by Holz and Co., N. Y. C. (too late for description here) which seems to embody a number of improvements. Special attention is paid to the illuminating system and the lenses.

A works microscope has been designed by Stead, primarily for the examination of large castings and forgings in place, in case it is impractical to secure microsections.[1] Illumination is secured from a small accumulator and incandescent lamp. This microscope is convenient and inexpensive and should be found extremely practical in works practice. The Campbell-Leitz microscope is also useful in this same connection, as the microscope tube can be attached to the base direct, and used similarly on large sections.

Binocular Microscopes.—Greenough binocular microscopes are now made by all of the leading manufacturers. They are particularly useful in examining fractures, the walls of cavities found in metals, crystals, crystal dendrites and small objects in general.

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[1] OSMOND and STEAD, "Microscopic Analysis of Metals," Sec. Ed., 1913, p. 121. A similar microscope is supplied by the Scientific Materials Co., Pittsburgh.

THE MICROSTRUCTURE OF METALS AND ALLOYS

We have seen, in the preceding chapter, that etching a micro-section of a metal shows it to be composed of numerous irregular grains or crystallites. Let us now consider the formation of such a structure by solidification from the molten state,[1] as well as the surface patterns which are obtained for certain typical alloys.

The Structure of Pure Metals and of Simple Substances. The process of crystallization from the liquid state is one which has been followed quite closely for a considerable number of substances, so that the mechanism of the process may be said to be farily well understood, speaking generally. It has been noted, by causing salts to crystallize from solutions on a glass slide, that crystals commence growing at points irregularly located but always at the cooler portions. Crystallization about these nuclei, as centers, then proceeds until further growth is arrested by the collision of neighboring crystals. In this way irregular points of contact are formed which depend in no way upon the crystal structure but which produce the irregular polygonal grains or crystallites.

The similarity of the granular structure of metals to the structure of foams and certain emulsions has suggested to some that there is a similarity in the mode of formation of these two types of structures. The "foam-cell" hypothesis, according to Professor Quincke, the originator, assumes the formation of two immiscible liquids at a temperature just above the freezing point. One of these liquids is present in large excess and forms the filling matter of the cells, while the other liquid forms the cell walls. The subsequent crystallization of the mass is then dependent

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[1] Those who are specially interested in this subject are referred to the First Report to the Beilby Prize Committee of the Institute of Metals on "The Solidification of Metals from the Liquid State," by Dr. C. H. DESCH, *Journ.* Inst. Met., 1914, No. 1, p. 57. This report is a comprehensive summary of the literature dealing with the subject, with the important exception of the work of PROFESSOR TAMMANN, to whose work reference will be made in the text. See also Dr. Desch's Second Report, *Journ.* Inst. Met., 1919, No. 2.

upon, and in strict accordance with, this "foam structure." In other words, according to this hypothesis, the subsequent granular structure of metals is determined, not by the conditions during solidification, but by the conditions prevailing prior to the formation of any solid whatsoever.[1]

Direct experimental evidence is against the foam-cell hypothesis as applied to the formation of the granular structure of metals; that is, observation not only does not indicate the formation of two liquids, which in itself would be difficult to explain physico-chemically, but it shows that crystals commence their growth at nuclei and proceed from there outward. Again observation teaches, as we shall see, that the crystallization of metals depends on the conditions which prevail *during* solidification. Desch has pointed out[2] not only the lack of quantitative tests of the correctness of this hypothesis but that as yet it has failed to produce an explanation of the geometrical properties of crystals, which certainly rest on a firm scientific basis.

Another method of forming a structure, very similar to the foam structure, is by the action of convection currents which are set up in cooling liquids. There has also been an attempt made to use this phenomenon to explain the formation of granular structure, but it too fails to satisfy for about the same reasons as just described. As Desch further points out, convection cells are always vertical, inasmuch as the currents are dependent upon gravity, so that they could not possibly form metal crystallites which grow in a direction perpendicular to the cooling surface.

We have in the work of Professor Tammann a satisfying exposition of the manner of solidification of metals from their melts, which is based on direct quantitative observations.[3] Tammann has shown that there are two steps in the crystallization of solids which are, namely, the formation of the crystal nuclei and the growth about these nuclei by the further depositions of solid matter. The exact method of formation of the so-called crystal nuclei is not definitely understood. It may be assumed that a nucleus forms as soon as a certain minimun number of atoms[4] ar-

[1] For a statement of this hypothesis by the originator, see the article by PROF. QUINCKE, *Intern. Journ. Met.*, 1913, Vol. 4, pp. 23, 79, and 303.

[1] *Loc. cit.*, p. 74.

[3] See TAMMANN, "Kristallisieren und Schmelzen," and "Lehrbuch der Metallographie," on which the present discussion is based.

[4] According to the recent work of Prof. Bragg, it would seem that the atom is the unit out of which crystals are built.

range themselves according to the space lattice characteristic of the solid phase.   But, according to Tammann, the formation of such a "constellation" of atoms is not sufficient to cause crystallization.   The atoms themselves must first of all change into an anisotropic state, whereby polar forces arise which hold the atoms in the space lattice.   This change is accompanied by an evolution of energy (heat).   This theory has received experimental support in the work of Othmer[1] who found that heating piperonal to temperatures considerably above the melting point lowered the nuclei number, due, supposedly, to the more extended conversion of the anisotropic atoms (or molecules) into isotropic atoms.   A somewhat similar effect has been described by Carpenter and Edwards[2] who found that remelting an aluminum bronze resulted in an increase in grain size.   These authors assumed from this that "the crystal units persist in what is probably a very mobile condition, at any rate for a certain range of temperature above the melting point," which, interpreted in terms of Tammann's theory, means the persistence of anisotropic atoms after melting.

It has been shown, furthermore, that the rate at which these crystal nuclei form is in accordance with a definite law which is the expression of the "force of spontaneous crystallization" for that substance at the temperature of solidification.   The measure of this force is to be had in the number of nuclei which form in unit volume and unit time at any temperature, which is called the "nuclei number."   This, Tammann has found to be relatively small immediately below the freezing point and to increase, with the degree of super-cooling, to a maximum somewhat below the freezing point.   This temperature range has been called by Ostwald,[3] the "region of metastability," because the melt, or liquid phase, can be retained as such at these temperatures for an indefinite length of time.   The addition of a small amount of the solid phase ("inoculation") supplies the nuclei necessary to produce crystallization and the entire mass solidifies at once.   This action may be explained, by the assumption of Tammann, that anisotropic atoms are able to convert isotropic

[1] *Zeit.* anorg. Chemie, 1915, Vol. 91, p. 209.

[2] Eighth Report Alloys Research Committee, *Proc.* Inst. Mech. Eng., 1907, Vol. 1, p. 164.

[3] See OSTWALD, "Lehrbuch der allgem. Chemie," 1896–1902, Vol. 2, Part 2, Sec. 1, pp. 379, 704.

atoms into anisotropic atoms and, so, to cause them to attach themselves to the space lattice of the existing structure. It has been found that at temperatures below the maximum, the value of the nuclei number again falls off.

The curve in Fig. 44 gives the general shape of the nuclei number-temperature curve, as determined for a number of salts which lend themselves readily to the investigation of this phenomenon. The value of the nuclei number for many sub- stances (silicates, and many salts) is so small, even at the maximum, that these substances can be read- ily produced in the amorphous state by rapidly chilling the liquid to room temperature. Metals, on the other hand, inasmuch as it has so far been impossible to chill them so rapidly as to inhibit crystalliza- tion, evidently have relatively high nuclei numbers.


Fig. 44.—A typical nuclei num- ber-temperature curve.

The temperature of the max- imum is, of course, independent of the nuclei number, and it may be either just below the freezing point or many degrees below.

The transformation of one solid phase into another solid phase proceeds in the same manner as just described. It has been found, for example, that the force of spontaneous crystal- lization, or transformation, of the change white tin = gray tin, reaches a maximum at about −50°C. At ordinary temperatures the tendency to form gray tin is so slight as to be negligible, which readily explains the relative stability of white tin through- out all but the coldest weather, although inoculation would cause the transformation to set in immediately.

The second step in the formation of the solid phase is the further crystallization about the crystal nuclei which have already formed. This, in individual crystals, does not proceed with the same velocity in all directions, otherwise the crystals would assume spherical shapes. On the other hand, the velocity of crystallization varies in different directions and must be regarded as a vector. It would be rather difficult to determine, experimentally, the velocity of crystal growth in the different

directions, but the average velocity can be readily determined and is called "the linear velocity of crystallization." This, like the rate at which crystal centers form, varies with the degree of super-cooling. At temperatures but slightly below the freezing point, the linear velocity of crystallization is comparatively small, but with drop in temperature it increases until it reaches a maximum value which, for the metals, is doubtless quite high.[1]

These two forces, represented by the nuclei number and the linear velocity of crystallization, determine the ease with which crystallization can be inhibited by rapid cooling, for it is evident that if the maximum nuclei number and the maximum linear velocity of crystallization are low, it would be comparatively easy to retain the liquid in the amorphous state. Inasmuch as this is not the case with the metals, it is apparent that the rate of formation of crystal nuclei (if not the velocity of crystallization as well) is quite high, at least at the maximum. While it is possible to super-cool molten metals, a value is always reached at the lower limit of metastability which is sufficient to produce crystallization, however rapid the cooling may be.

The Grain Size.—According to Tammann the relationship between the grain size and the two forces of crystallization may be summed up as follows: The occurrence of crystallites in irregular sizes points to a low rate of formation of crystal centers, because the distance between crystal centers in that case will be very accidental. This is so particularly if, at the same time, the linear velocity is large. If, however, the linear velocity is small at the same time, there will be a correspondingly smaller variation in the size of the crystallites because the time of crystallization is correspondingly increased. A small uniform grain size points to a high rate of formation of crystal centers.

An attempt to determine the value of the force of spontaneous crystallization from the microsection has not led to definite results. If n is the number of polygons on the surface of the specimen whose area, measured in square centimeters, is q, then the number of crystallites in one cubic centimeter is

$$N = \left(\frac{n}{q}\right)^{3/2}$$

The determination of N gives only an approximate idea of the

[1] An extended discussion of this factor is given by TAMMANN, "Lehrbuch," p. 8.

force of spontaneous crystallization because the nuclei number varies during solidification, making the relationship between N and the nuclei number complex instead of simple.

Some experiments on antimony and bismuth, intended to show the relationship between the nuclei number and the degree of super-cooling, have been carried out by Bekier.[1] He showed, apparently, that the nuclei numbers of these two metals vary in a different manner and it is quite probable that this method of treating solidification from the molten state will utimately lead to important results.

Nuclei Number and Linear Velocity
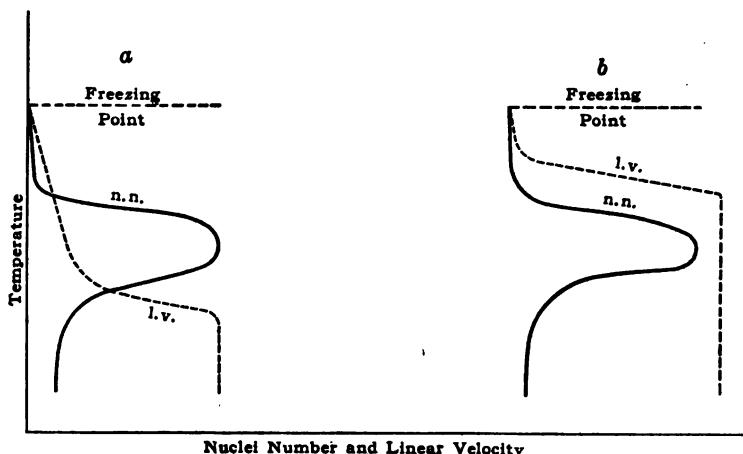
FIG. 45.—Two possible relations between the nuclei number and the linear velocity curves.

We have yet to consider the effect of the rate at which heat is extracted from the substance during solidification, or the rate of cooling, whether slow or rapid. In Fig. 45 are shown two possible combinations of the nuclei number-temperature, and linear velocity-temperature curves. At (a) the maximum nuclei number comes at a higher temperature than the maximum linear velocity. Under these circumstances a large number of nuclei form but are unable to grow to any extent until a lower temperature is reached. At the lower temperature crystal growth proceeds very readily under conditions most favorable to crystallization. If the cooling is fairly slow a large number of nuclei form at the higher temperature which immediately grow into

[1] *Zeit.* anorg. Chemie, 1912, Vol. 78, p. 178

crystallites as soon as the temperature falls to that of the maximum of the linear velocity. Slow cooling under these circumstances tends to produce a relatively fine structure. Rapid cooling, on the other hand, would bring the melt, with a correspondingly smaller number of crystal nuclei, more quickly to the region of maximum growth and the tendency would be to form a smaller number of larger crystallites.

At (b) the maximum nuclei number lies within the zone of maximum velocity of crystallization. Under these circumstances slow cooling should not produce as fine a grain as at (a) but rapid cooling should produce a finer grain than slow cooling. Needless to say, this case is the common one for it is generally true that a chilled metal shows a finer grain size than a slowly cooled metal. The conditions here are probably not as simple as are represented by the two curves because the tendency to crystallize opposes the tendency to form crystal nuclei. This would have its effect on both values.

Having considered the forces governing the crystallization of metals, we shall next take up the manner of growth of the crystallites and their microstructure.

Lehmann, in his book on "Molecular Physics,"[1] points out that crystal growth proceeds only in a supersaturated solution, and that the saturation is greatest at points and sharp angles where the replenishment of material, due to the "concentration currents," is greatest. If the liquid is a molten metal, its degree of saturation is determined by its temperature, which, Lehmann points out, will also be lowest at the sharp points, due to the flow of the latent heat of solidification. This selective deposition gives rise to an elongated axis, a system of secondary axes set up at right angles to it, and other systems of axes of a higher order, all of which maintain a constant inter-axial angle. This structure is known as "dendritic," or "Christmas tree" structure, and is quite common to crystal formation. At times, however, it is rather difficult to recognize it, if the "filling in" of the interstices keeps pace with the dendritic growth. It is not necessary for the dendritic axes to coincide with the crystallographic axes. They do in the case of the octahedron but do not in the case of the cube, which are two of the more common forms found among the metals.

This style of crystal growth is represented diagrammatically

[1] See also, LEHMANN, "Die neue Welt der flüssigen Kristalle," 1911, p. 67.

in Fig. 46. The solid lines represent cross sections of the axes of solidification which, on further growth, will ultimately form the crystallites represented by the dotted polygons. The

FIG. 46.—Diagrammatic representation of the mode of crystal growth—dendrites.
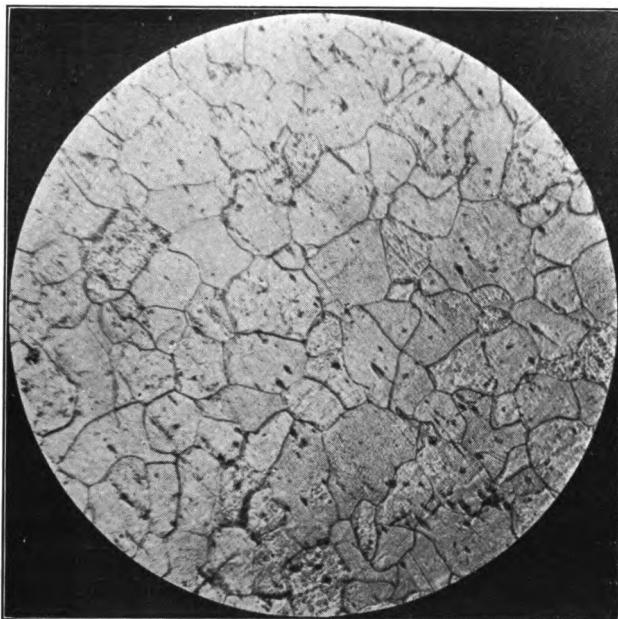

FIG. 47.—Polygonal structure in pure iron. (*Jeffries.*)

background represents the mother liquor or molten metal in which the crystals are growing. Chemically, each crystal is homogeneous because the successive depositions of solid are all of the same composition. Consequently, on etching a micro-
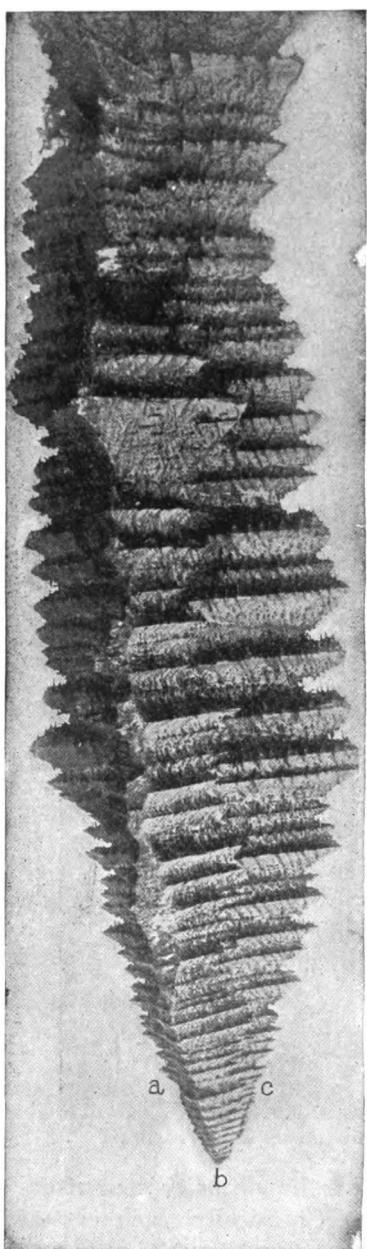
FIG. 48.—Dendrite of steel. (*Tschernoff.*
By permission of Dr. Howe.) ×½.

section, the effect produced is simply that of differential corrosion, as discussed above, and the manner of crystal growth is not revealed. A typical structure is shown in Fig. 47 which is the photomicrograph of a piece of pure iron.

Crystallites which form in cavities or on the surface have the opportunity of growing unobstructed by neighboring crystallites, but instead of forming crystals with well-developed faces, they generally assume an exterior form which is characteristic of the dendritic structure. The crystallites are then called "dendrites." This structure is shown in Fig. 48.

To develop the true crystalline nature of metals, Heyn, Stead, Osmond, and others, took advantage of the variation in the rate of attack of etching reagents with the crystallographic orientation. Thus when a microsection is treated with a suitable etching reagent[1] for a somewhat longer time than is customary, the crystallites are eaten away in a manner that clearly dem-

[1] Copper ammonium chloride and picric acid are used for "deep etching."

1 gm. picric acid to 100 c.c. alcohol is used cold; time 1–4 hr.

1 gm. picric acid to 25 c.c. alcohol is used at 100°C. for 1–5 min.

onstrates their anisotropic character. This method is known as "deep etching." The effect of deep etching on an alloy of iron and silicon, which here behaves like a pure metal, is shown in Fig. 49 which is due to Stead.

This is, in fact, what happens every time a microsection is etched but the effect is much less pronounced and rarely becomes evident. If the section is only lightly etched, the polygonal structure is developed and the crystallites appear uniformly light with dark borders. If the etching is carried a step further, minute crystal facets are developed giving the appearance in
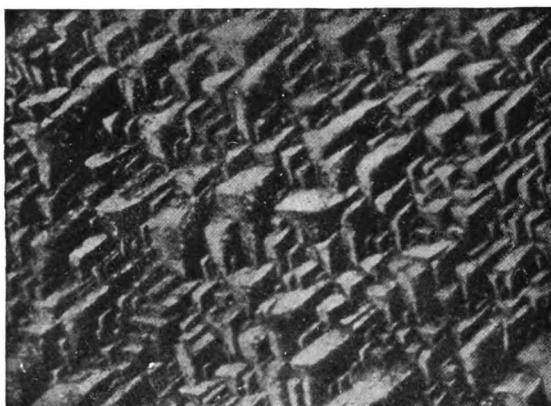
FIG. 49.—Rectangular etching cavities in silicon steel. (*Stead. By permission of Dr. Howe.*)

Fig. 50. The different shades in the different polygons are due to the variation in the orientation of the facets, and are commonly referred to as "oriented lustre." This phenomenon can be studied much more advantageously under oblique illumination,[1] which produces a truly brilliant effect. By rotating the stage, the lustre of the crystallites changes from light to dark and vice versa, as the orientation of the facets changes relatively to the direction of the light. By carrying the etching one step further, as in deep etching, the facets become coarse as in Fig. 49. All these effects are taken as direct evidence of the crystalline nature of metals.

There is still another "etching effect" which depends on crystalline structure, *e.g.*, "etching pits," which are minute cavities

[1] The Rosenhain microscope, with a rotating stage and oblique illuminators, has been specially developed for facilitating this examination.

formed on the surface of the specimen by the corrosion of the etching reagent. These may be seen in Fig. 51, which is a section of iron rather deeply etched. In any one crystal, the sides
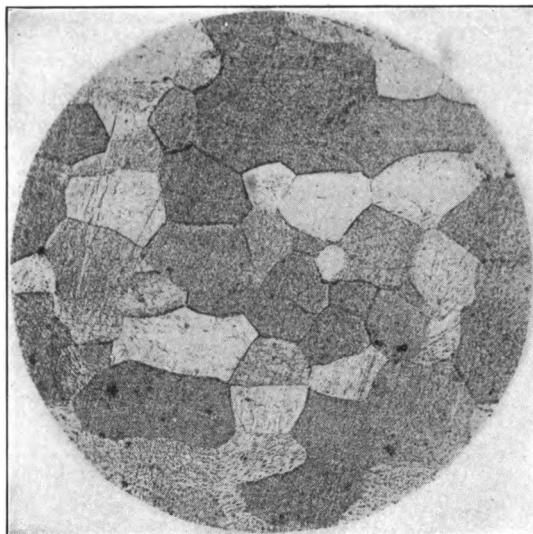

Fig. 50.—Polygonal structure in pure tungsten. Oriented lustre. (*Jeffries.*)
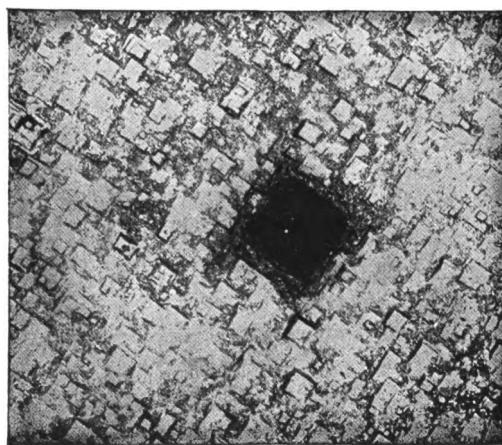

Fig. 51.—Etching pits in steel. (*Stead. By permission of Dr. Howe.*)

of the pits are all parallel, but in neighboring grains, the direction changes.

A somewhat similar effect is produced by casting metals on

glass, when entrapped bubbles of air form so-called "negative crystals," which again demonstrate the crystalline texture of metals.

Twinning.—Metallic crystals exhibit "twinning" much the same as the minerals. The effect, as viewed under the microscope, is shown in Fig. 52. It is observed that part of the bands are light and the remainder are dark. On rotating the stage, the light bands become dark, and the dark bands become light, which shows the definite relationship between the orientation of the two sets of bands.
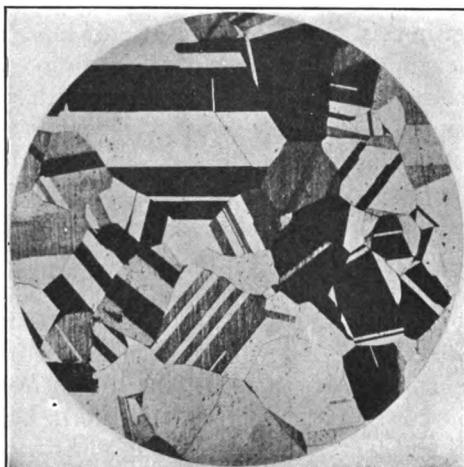
FIG. 52.—Twinned crystals of brass. × 50. (*Mr. F. G. Smith.*)

Structural Changes at Transformation Points.—That structural changes accompany polymorphic transformations, has already been made clear under the discussion of sulphur and tin. Other metals undergo transformations of this character, but the structural changes are generally less pronounced; in fact it is usually impossible to distinguish between the different allotropes by a microscopic examination. The chief change in microstructure is in the grain size, which takes place according to the principles already discussed.

It would be impossible to offer a complete discussion on the crystallization of metals from the liquid state, without including the "amorphous cement" theory which is due principally to Rosenhain and his collaborators. This theory, which seems to

have been originally introduced by Brillouin[1] (Desch, First Report) is based on the idea that the atoms which find themselves between the crystallites during the final moments of solidification are unable to attach themselves to either space lattice and so are forced, on cooling down, into the amorphous state. Apparently this hypothesis assumes no change in the atom (*i.e.*, isotropic-anisotropic) on crystallization so that the material between the crystallites is regarded as being truly amorphous and isotropic. How this is to be reconciled with Tammann's theory of the influence of anisotropic atoms on isotropic atoms is not made clear.

No claim is made for this theory that it is to be accepted as one based on experimental proof, but it is offered more as one which is capable of explaining a number of hitherto loosely correlated phenomena. As such it has been eminently successful and has been accepted by numerous metallographers as a working hypothesis. As remarked by Heyn, the assumption of the occurrence of metals of the amorphous state, whether due to incomplete crystallization or to mechanical deformation (as we shall see later) is an hypothesis and, like all other pure hypotheses, cannot be controverted. On the other hand, there are many metallographers who feel that direct experimental proof of the existence of the amorphous envelopes surrounding the crystallites, should be advanced before the theory can serve a truly useful purpose; in other words it should be borne clearly in mind that the hypothesis may be wrong and that the true explanation may be entirely different.

The hypothesis, as first advanced in detail by Rosenhain and Ewen,[2] assumes that the interstices between the crystallites are smaller than the crystal units, so that the "liquid molecules" contained within the space are forced to remain in the liquid or amorphous condition. According to this it would appear that the cementing material is supposed to be of molecular thickness. An amorphous cement of molecular dimensions is not of sufficient thickness to explain what it is attempted to explain by this hypothesis (Rosenhain) and it has been advanced that the cement is probably of the order of magnitude of 100 molecules (Jeffries). Thus the hypothesis, to be tenable, requires an appreciable thickness to the layer of cement, and yet it seems reasonable to suppose that any excess of free molecules would readily attach them-

[1] *Ann. Chim. et Phys.*, 1898 (VII), Vol. 8, p. 377.
[2] *Journ.* Inst. Met., 1912, No. 2, p. 149; 1913, No. 2, p. 119.

selves to the nearest crystalline unit and so limit the thickness to molecular dimensions (Guertler).

The Microstructure of Binary Alloys.—In Chapter I it was stated that pure metals, solid solutions, intermetallic compounds and even mechanical mixtures form during the solidification of binary alloys. A satisfactory discussion of all the factors operating to influence the microstructure, or "surface pattern," as these constituents crystallize, is not only impossible at the present time, due to our lack of information in many cases, but would be outside the scope of the present work. Here we shall have to do only with the more evident influences, principally
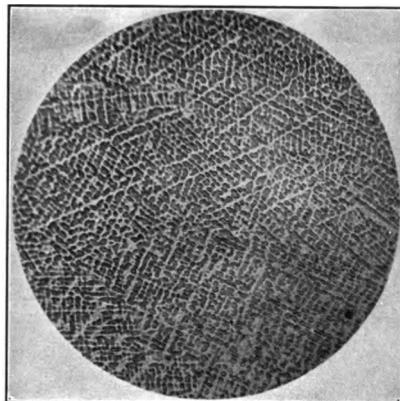
Fig. 53.—Dendritic structure in a solid solution. × 66.

the genesis of the alloy as determined by its location in the binary series of which it is a member. Perhaps the simplest method of procedure, is to discuss the microstructure of binary alloys according to the different types of constitution diagrams noted above. In this way, the close relationship between the microstructure and the constitution diagram, will become apparent.

Solid Solutions.—During the solidification of a solid solution we have conditions which may (and usually do) lead to a different microstructure than that of pure metals. This is due to the fact that the composition of the solid changes continually during solidification and that, unless the cooling is very slow, the dendritic cores will differ in composition from the filling matter. The actual variation will depend on the rate of cooling, or on the time available for the inter-diffusion of the two metals after being deposited. This difference in chemical composition

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gives rise to a typical microstructure, known as "dendritic structure," which is due to a differential coloring of the core and the filling, as shown in Fig. 53.[1]

The dendritic orientation is constant in any one grain or crystallite but, of course, varies from grain to grain. If a structure such as is shown in Fig. 53, is reheated to a high temperature, sufficiently high to permit through diffusion, the attainment of chemical homogeneity, the core or dendritic structure will disappear and the appearance of the alloy will correspond to that shown in Fig. 47. In the same way, if the cooling is very slow, the composition of the solid phase follows the solidus and so keeps pace with the drop in temperature, an assumption which was made for the discussion in Chapter I. This results in an aggregate of crystallites, whose composition at all points corresponds to the total composition of the alloy. The microstructure of such an alloy is similar in every way to that of a pure metal.

Eutectic Structure.—The binary diagram shown in Fig. 6 will be taken as a basis for this discussion. The microstructure of the alloys within the α and β fields corresponds to that just described so we shall pass at once to a consideration of the eutectic which is a mechanical mixture of the two phases α and β.

Fig. 54.—Eutectic solidification.

The following discussion is intended to explain, in a simple manner, the mechanism of the formation of the eutectic structure and utilizes Tammann's conception of crystallization. In some respects it differs from the argumentation which is usually given on this point.
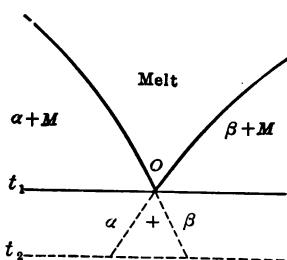
For the purposes of the present discussion, the eutectic point has been drawn to a larger scale in Fig. 54. We know that α and β are in equilibrium with the melt at t_1, and therefore, from the phase rule, that the eutectic should solidify at constant temperature. But we also know that crystallization proceeds only in supersaturated solution, so that the temperature of the melt will drop to some temperature t_2, slightly below the eutectic

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[1] The history of the genesis of the crystallites, as depicted by their microstructure, has been advanced as evidence to controvert the "foam-cell" hypothesis (Rosenhain).

temperature t_1, before the deposition of any solid takes place. On doing so the melt becomes supersaturated with respect to both solid phases. The formation of the two solid phases at this point depends on an intensity factor which is determined largely by the nuclei numbers of α and β and probably to a lesser extent by the linear velocities of crystallization.[1] The rate of cooling can have a secondary influence by determining the temperature of solidification and therefore the actual values of the nuclei numbers and velocities of crystallization of α and β which are actually in force.

There are just two cases possible; either the nuclei numbers must be approximately equal to each other, or they must be different. Under the conditions of the first case, we would expect a simultaneous separation of α and β. This does not mean that the nuclei of α and β would form at the same place, or in contact with each other, although local temperature variations might lead to such a deposition. At any rate, crystals of α and β would form, independently of each other, throughout the cooler portions of the melt. There would be no appreciable change in the composition of the melt, but there would be, rather, according to Vogel, a "differentiation" of the liquid into α and β. If the nuclei numbers of α and β are different, one or the other would separate first, and in that way produce a local variation in the composition of the melt. Assuming an appreciable velocity of crystallization, or deposition of solid about the nuclei, the local concentration would vary until the deposition of the second constituent is caused. It is not necessary to assume, even here, that the deposition of the first constituent is completely inhibited although it may be appreciably retarded. So by either simultaneous or periodic and alternating deposition of the solid, the solidification of the eutectic proceeds.

There is no reason to believe that the conditions during eutectic solidification remain constant; in fact, it seems quite possible

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[1] Inasmuch as we are dealing with the metals which have a strong tendency to crystallize, at least as soon as nuclei form, we would expect the relative velocities to have an appreciable influence only in case there were considerable difference, in this respect, between α and β. As for the values of the linear velocity, it has been shown that they are influenced by the presence of second substances, and they may be well considered to vary during solidification if the composition of the melt varies, as certain signs seem to indicate. See Moore, *Zeit.* Phys. Chem., 1893, Vol. 12, pp. 545, 559; and Bogojawlinsky, *ibid.*, 1898, Vol. 47, p. 585.

that slight temperature and concentration variations can lead to variations in both grain size and in the relative amounts of the constituents which are deposited. For example in Plate IV-*A*, of Desch's Metallography, p. 185, the copper-copper phosphide eutectic appears to have formed, at the start, a fine-grained aggregate with a preponderance of the dark constituent and a coarse-grained aggregate with a preponderance of the light constitutent, during the later stages of solidification.

Vogel, after studying various eutectic structures, came to the conclusion that eutectic solidification proceeds by the simultaneous separation of the constituents, although one, by reaching its maximum nuclei number at a lesser degree of super-cooling than the other, may continually form a trifle in advance and so play the leading rôle in determining the surface pattern.[1]

From the microscopical examination of eutectic structures, it is apparent that, whatever the cause, one of the constituents may have a predominating influence in forming the structure. This constituent is sometimes referred to as the "predominant partner" (Rosenhain). This leading constituent possesses the superior "power of orientation" (Desch) and so crystallizes more or less independently, and forces the other one to solidify in the space left. Various theories have been advanced to account for the predominant partner, among which are that it is the constituent with the greater "ability to form extended crystal skeletons" (Desch), that it is the harder constituent (Stead) and that it is the constituent present in a larger proportion by volume (Rosenhain).

The structure or surface pattern of the eutectic depends very largely upon these factors and inasmuch as the forces of crystallization, both absolute and relative, vary from system to system it is natural that alloy eutectics present eutectic patterns which are quite varied in appearance. According to the surface pattern we may classify eutectic structures, according to the arrangement of the lamellæ, as curviplanal, rectiplanal, and honeycombed or cellular (Stead).

These three characteristic eutectic structures are shown in Fig. 55. At *a* the two constituents occur as alternate lamellæ so that it is plausible to assume that neither constituent has a predominating influence. At *b* is shown the curviplanal or fan-like structure. In this case it seems as if, in contrast to case *a*, the conditions affecting the structure had varied during

[1] *Zeit.* anorg. Chemie, 1912, Vol. 76, p. 425.

solidification with the result that one constituent grew more rapidly during the final stages and so had produced the fan-like structure.   At *c* we have the cellular type which is decidedly due to one constituent.   It, the "predominant partner," tends
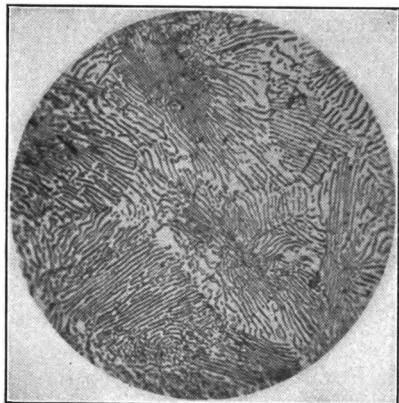
a
Rectiplanal.   Eutectoid in steel.   × 530.
(*Hanemann.*)
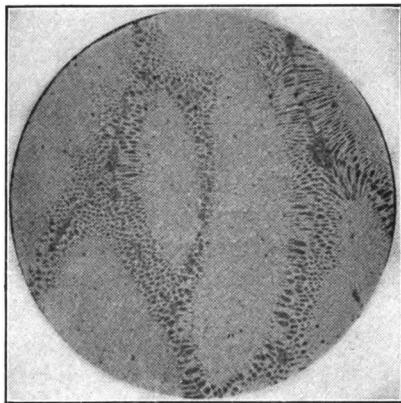
b
Curviplanal.   Zinc-cadmium eutectic.   × 33.
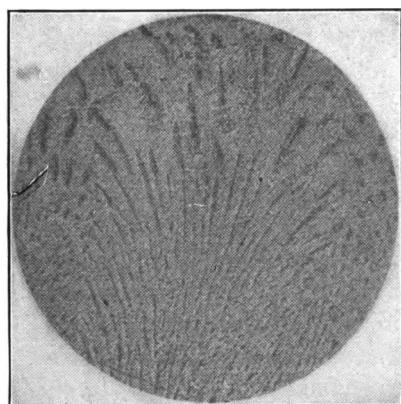
b
× 270.
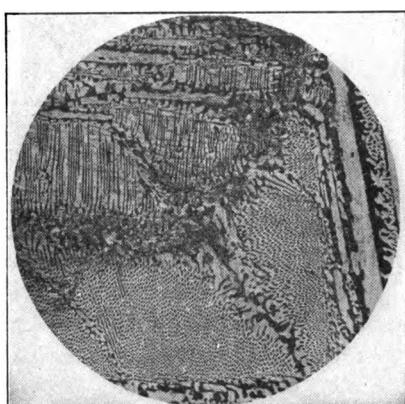
c
Cellular.   White iron eutectic.   × 80.
(*Leitz.*)

Fig. 55.—Eutectic structures.

to form regular crystals and encloses the other constituent in the form of rods as a bundle of matches.

One of the characteristic features of eutectic structure is the formation of cells or what Benedicks has termed "colonies."

These are readily apparent under low magnification, and frequently have an appearance somewhat similar to the polygonal structure of a pure metal, and might be mistaken for such. It is only under higher magnifications that the true structure is apparent. In the hand specimen, the microsection exhibits a pearly luster much like that of mother of pearl, due to the refractive action of the minute lamellæ.

If the composition of the eutectic is quite close to that of one of the phases, the pattern will be determined by the phase which is in excess. In fact, the minor phase exists simply in between the grains of the predominant phase so that the characteristic eutectic structure is lost. As the limiting case, the composition of the eutectic may coincide with one of the pure metals, as in the case of the copper-lead series.

Microstructure of the Alloys Consisting of α + Eutectic. The primary α solid solution crystallizes in the melt subject to the influences already discussed. It forms crystal skeletons or dendrites as the temperature falls, while the melt, whose composition continually approaches the eutectic concentration, reposes in the interstices. The chief difference between this case and the crystallization of a pure metal in its own melt, is that crystallization proceeds both with drop in temperature and with change in composition of the two phases, which factors also influence the forces of crystallization.

The solidification of the eutectic rest is apt to differ from that described for the free eutectic inasmuch as it is now impossible to super-cool the melt with respect to the α phase. However, if the β phase fails to form at t_1, the α phase continues to form at temperatures below t_1, until the β phase does form. The primary α crystals may play a very important rôle in determining the surface pattern in the neighboring colonies by determining the form and crystallographic orientation on the small α crystals. In this way the α phase can become the predominant partner, even though the tendency, otherwise, may be in favor of the β phase. Desch cites the eutectic Sb-Cu$_2$Sb to illustrate this point. The eutectic, in the vicinity of primary antimony crystals, shows triangular antimony crystals, all oriented similarly to the large antimony crystals, embedded in Cu$_2$Sb. The eutectic at greater distances from (*i.e.*, influenced by) the antimony crystals has a surface pattern which is characteristic of neither constituent.

The same discussion would hold good for the alloys consisting

of primary β and the eutectic, but it should be pointed out that the eutectic structure is liable to be different on one side of the eutectic point from that on the other side, for reasons which have been made clear.

The relative amounts of primary constituent and eutectic can be determined by use of the lever relationship. To do so, the compositions of the eutectic and the primary phase are used as the ends of the lever arms and the total concentration as the fulcrum point. This rule shows that the amount of eutectic increases from the composition of one of the phases, to the eutectic point, where it is 100 per cent. of the alloy, and again decreases to zero at the composition of the other phase. This principle is used in commercial laboratories to determine the amount of oxygen in commercial copper and the amount of carbon in steel.

The usual effect of surface tension on the shape of the primary crystals is to produce dendrites with rounded surfaces, which shows that the surface tension is greater than the resistance of the material. The diamond has been cited as an example of this effect (Tammann). On the other hand, if the strength of the material exceeds the force of surface tension, the dendrite is able to assume its more natural shape, often characterized by sharp angles. F, the resistance of the material, decreases with rise in temperature, while α, the surface tension, increases, so that if the liquids pass through the temperature corresponding to $F - \alpha = 0$, the structure of the primary phase varies according to its temperature of formation. The alloys of copper and bismuth, and of iron and silicon, may be cited as exhibiting this effect (Tammann). A copper dendrite which has formed at a low temperature, is shown in Fig. 56. At this temperature the effect of surface tension is not great enough to round off the sharp angles.

The Microstructure of Eutectoids.—Eutectoids, as will be remembered from the discussion in Chapter I, are mechanical mixtures of two phases, corresponding to eutectics, but which form in the solid state. Such being the case, it is not surprising that the structure assumed by the eutectoid is very similar in appearance to that of the eutectic so it will be difficult to distinguish, off hand, between the eutectoid structure and the eutectic structure. This was originally a source of confusion to metallographers; for example, the eutectoid in the copper-

tin alloys was formerly regarded as forming from the melt. Campbell[1] quenched the alloys from successively higher temperatures and was able to demonstrate that the structure formed "in the solid," *i.e.*, it formed by the breakdown of a solid solution.

Whereas it has been impossible, as yet, to suppress the eutectic reaction, it is readily possible to cool so rapidly through the temperature of the eutectoid inversion, that the high temperature modification is retained intact, a common example of which is the retention of the β constituent of either the copper-tin or copper-aluminum series by quenching in water.
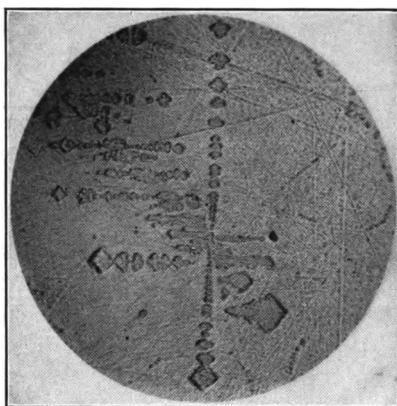
Fig. 56.—Copper dendrite in a bismuth-copper alloy.   × 66.

The Microstructure of Type III Alloys.—The characteristic feature of these alloys is the peritectic reaction between the solid and the melt.   The primary α phase crystallizes in the form of dendrites while the melt is present as intersticial filling.   At the peritectic temperature the solid and melt react to form the new solid at the surfaces of contact between the dendrites and the melt.   If the reaction is completed, we have, as the resulting microstructure, the α dendrites, only partially filled out, and the β phase as the matrix or filling matter.   If the diffusion is insufficient to permit the completion of the reaction, "reaction rims" are formed which interfere with and at times even inhibit the reaction.   This is a common case and has been discussed quite

[1] See Appendix to the Fourth Report to the Alloys Research Committee; *Proc.* Inst. Mech. Eng., Dec. 20, 1901, p. 1218.

thoroughly by Guertler[1] who shows that one or even more phases can form in successive reactions and persist at room temperature in a metastable condition. An example of an alloy which is in an unstable condition, due to the presence of a reaction rim, is shown in Fig. 57. In this alloy there are two constituents which etch light and one which etches dark. The reaction between the primary dendrites and the melt has produced a second phase which completely surrounds the dendrites. After proceeding a certain distance, the reaction stopped, and the dark phase formed during final solidification. In *b* the three phases can be seen clearly. The formation of reaction rims is not limited to changes
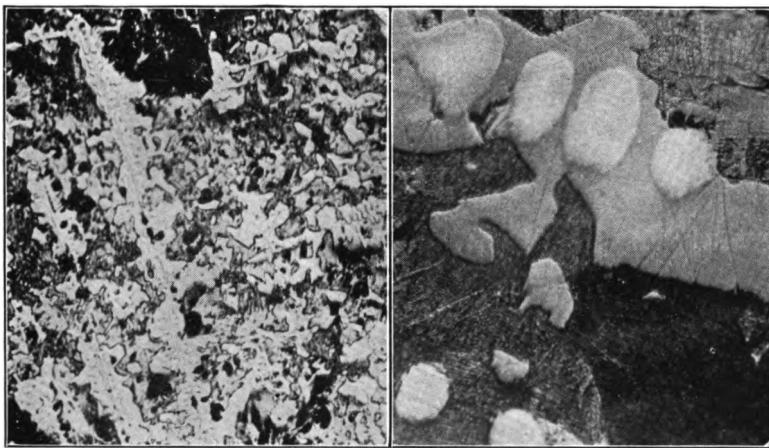
a ✕ 100. *b* ✕ 800.

FIG. 57.—Incomplete peritectic reaction; bismuth 72 per cent., nickel 22 per cent.

going on during solidification but may also extend to transformations in the solid state. An occurrence of this nature, which was noted by the author in alloys of copper, tin and zinc, is shown in Fig. 58. A more complete description is to be found in the *Trans. Amer. Inst. Min. Met. Eng.* for 1918.

If the melt is in excess, the α dendrites are all used up in the reaction and the resulting microstructure is simply that of the β solid solution. Here again, however, we can have an incom-

[1] *Metallographie*, Vol. I, Pt. 1, pp. 277–296. The peritectic reaction at 800°C. in the Cu-Sn alloys is an example of the former case and that at 400°C. of the latter. See HAUGHTON, *Journ.* Inst. Met., 1915, Vol. 13, p. 222.

plete reaction and the resulting unstable structure as described above.

The microstructure of the alloys consisting entirely of the α
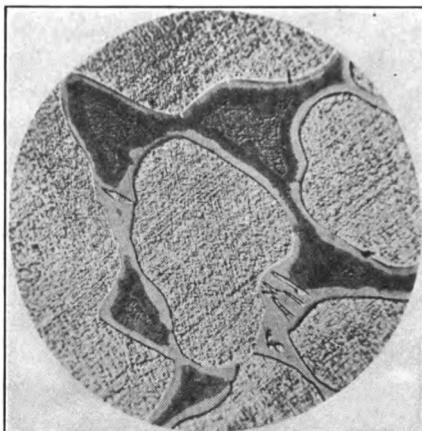
Fɪɢ. 58.—Reaction rim in a copper-tin-zinc alloy.   × 530.

or the β solid solutions is the same as of any solid solution and requires no special mention here.

Segregates.—Many times a solid solution, either on heating or cooling, becomes supersaturated with respect to one of its
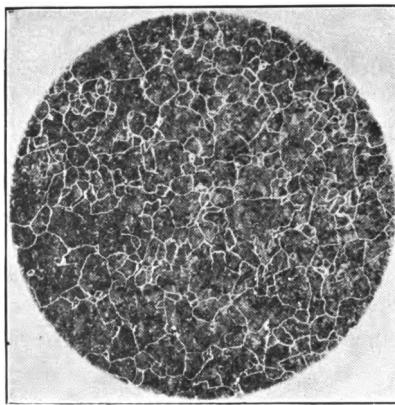
Fɪɢ. 59.—Network structure in steel.   × 5.   *(Foley.)*

components.   This occurrence can be seen at a glance from the constitution diagram, as in this case the concentration vertical passes from the field of the solid solution into a field of that phase

plus another phase. This gives rise to the formation of the new phase, known here as a "segregate." The segregate forms, first of all, along the crystal borders of the old phase so that a section, polished and etched, has the appearance shown in Fig. 59. This structure is sometimes called a "net work" structure.

If the amount of the segregate is somewhat in excess of that shown in Fig. 59, the new phase forms, not only along the crystal borders, but also along the cleavage planes of the crystals of the old phase. The structure produced is shown in Fig. 60a. This structure was first observed in meteorites in 1808 by Alois de Widmanstätten and is called after him "Widmanstättian struc-

<p style="text-align:center;">

       a   *b*
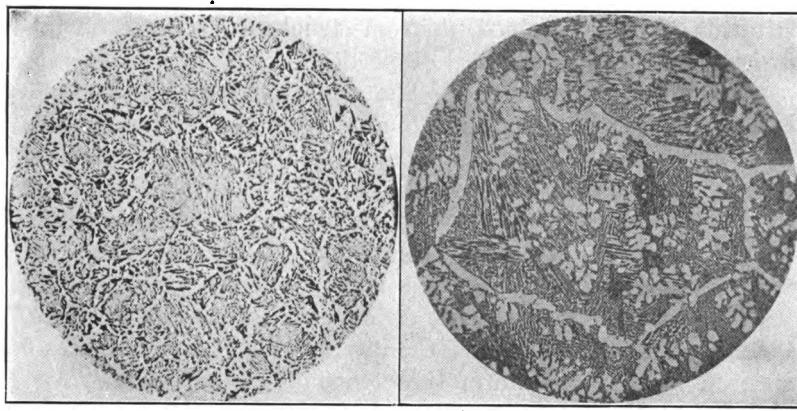
Fig. 60.—Widmänstattian structure. × 66.   Segregate structure. × 270.
(*Hanemann.*)
</p>

ture."[1] The appearance is very distinctive and is met with repeatedly among the metallic alloys. According to Belaiew, "the appearance of these Widmanstättian figures is connected with two fundamental facts—the character of the primary octahedral crystallization,[2] and the separation of the solid solution into different phases during recrystallization."[3]

Widmanstättian structure is of scientific interest inasmuch as it is regarded as an indication of the crystalline structure of the

[1] BELAIEW, "The Widmanstätten Structure in Various Alloys and Metals," *Journ.* Inst. Met., 1914, Vol. 12, p. 46.

[2] It seems to be generally agreed that the term applies in case the segregate forms according to any crystallographic orientation, even those other than the octahedral.

[3] *Loc. cit.*, p. 48.

solid solution in which, or out of which, the segregate forms. It has been made the subject of study by various authors, but notably by Belaiew.[1]

Widmanstättian structure is important in technical metallography as being an indication of weakness and lack of toughness. It is most commonly found in steel castings, and in forgings which have been finished at too high a temperature, but is also observed in brass and bronze and in other non-ferrous alloys in which segregates form. Under these circumstances, it is commonly known as "casting structure." This structure can be removed, in most cases, by suitable heat treatment, but at times it is necessary to resort to mechanical work. In all cases, the substitution of a fine grained, unifrom structure results in an improvement in the mechanical properties.

Intermetallic Compounds.—The appearance of intermetallic compounds is not materially different from that of pure metals or of homogeneous solid solutions; therefore, a simple examination under the microscope will not, as a rule, give sufficient evidence upon which it may be determined whether or not a constituent is an intermetallic compound. If the compound is of the type given in Fig. 8, that is, one which forms eutectics with the two pure metals, the examination of a series of alloys, including the composition of the intermetallic compound, shows that as the composition of the compound is approached from either side, the eutectic gradually disapears until at the composition of the compound, the structure is homogeneous. In this manner the presence of the compound is revealed.

The presence of an intermetallic compound, which forms on the reaction between solid and melt, as in Fig. 10, may also be detected by the examination of the series. At the composition of the compound the alloy will be perfectly homogeneous. The microscopical identification of this alloy as an intermetallic compound rests upon the fact that the alloy is of simple atomic proportions and is homogeneous. For more positive identification the physical properties may be considered, which, as we shall see later, give more positive proof. If three phases are seen to be present under the microscope, as in Fig. 57, at least one is known to be unstable, and it becomes necessary to allow the reaction

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[1] "Rev. de Metallurgie," 1910, p. 510; 1912, p. 321. See also BENEDICKS, International Congress for Mining, Metallurgy, etc., Düsseldorf, 1910.

to complete itself by annealing at a temperature just below the reaction temperature.

There are occasionally certain features which are of assistance in identifying a constituent as an intermetallic compound, such as color, crystal form, etc., in which the constituent differs conspicuously from the pure metals. Examples are Al_2Au which is purple and Cu_2Sb which is violet. The compound Mg_2Pb is also very characteristic and is at once recognized as an intermetallic compound. In all cases the composition of the compound must correspond to some simple atomic relationship, which, however, need not correspond to valencies of the elements as generally used in chemistry.

FIG. 61.—Platelets of Fe_3C in white cast iron. (*Hanemann.*)

Desch, who has made a special study of intermetallic compounds,[1] remarks that when a "compound is accompanied by a eutectic, its development often differs in a marked degree from that of a single metal. The tendency to form crystals with plane faces, like the crystals of salts deposited by an aqueous solution, instead of skeletons, is much more pronounced among intermetallic compounds than among the metals. The crystallographic constants of a few only of such compounds have been observed, but a rhombic habit certainly predominates. In general, it may be said that the symmetry of the compound is lower than that of its components. Cubic forms are rare, and such

[1] See C. H. DESCH, "Intermetallic Compounds."

apparent cubes as are observed are probably less simple crystals, having a pseudo-cubic habit." Desch further points out that compounds may crystallize in simple rhombs if present in small excess over the eutectic composition, but that they form characteristic skeletons when in larger excess. This is true, even with a compound like PbS, ordinarily of a very pronounced crystalline structure but which may form well rounded dendrites when crystallizing from a melt. The characteristic microstructure of the compound Fe_3C, which is found in the high-carbon (hypereutectic) white cast irons, is shown in Fig. 61. The platelets of Fe_3C are embedded in the eutectic.

It is evident then that the microstructure of metals and alloys prepared by fusion and allowed to cool to room temperature offers a very good index to the genesis of the microconstituents. In this connection, the principal structures encountered are, in the case of pure metals, the polygonal and dendritic, and of binary alloys, the dendritic and polygonal, the peritectic and eutectic (eutectoid) and segregate structures, the latter occurring as net-work, and Widmanstättian, or casting structures.

CHAPTER V

PYROMETRY AND THERMAL ANALYSIS

Pyrometry, as discussed here, has reference particularly to the measurement of high temperatures and to thermal analysis as carried on in metallographic laboratories. This discussion concerns commercial pyrometry only so far as the latter shares points in common with laboratory practice.

The measurement of temperature must necessarily depend upon the measurement of some physical constant, such as the dilatation of a column of mercury, whose variation with temperature has been determined. From this measurement the temperature of the body in question, expressed in degrees of an arbitrary scale, is obtained. From the nature of these measurements it is necessary to use an arbitrary temperature standard, the one generally employed being the so-called "gas scale," which is in turn based upon the assumption that the equilibria ice-water, and water-water vapor, occur at 0°C. and 100°C. respectively at a pressure of 760 millimeters.

From the laws of Gay-Lussac ($v_1 = v_0 (1+\alpha t)$ at constant pressure), and Boyle, ($p_1 v_1 = p_o v_o =$ Constant, at constant temperature), it is known that $p = p_o (1+\alpha t)$ if the volume remains constant,[1] where α is the coefficient of expansion for perfect gases and is equal to 0.00367 or $\frac{1}{273}$. According to this equation, the pressure increases in a definite manner with the temperature. This is the principle of the constant volume nitrogen thermometer, by means of which the gas scale has been accurately determined

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[1] Leaving the pressure constant, equal to p_o, we have $v_2 = v_o (1 + \alpha t)$ by raising the temperature. Leaving the temperature constant, we have, in turn, $p_o v_2 = p_1 v_1 = p_o v_o (1 + \alpha t)$, by increasing the volume. It follows then that

$$p_1 v_1 = p_o v_o \left(\frac{273 + t}{273}\right) = p_o v_o \frac{T_1}{T_o} \text{ or } \frac{p_1 v_1}{T_1} = \frac{p_o v_o}{T_o}.$$

If the volume remains constant

$$p_1 = \frac{p_o T_1}{T_o} = p_o \left(\frac{273 + t}{273}\right) = p_o(1 + \alpha t).$$

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at the larger laboratories. It is by comparison with the readings of the nitrogen thermometer that the scales of other thermometers or pyrometers are ascertained.

Mercury Thermometers.—Mercury thermometers are but infrequently used in metallographic laboratory practice, except for perfectly general purposes. Their bulk and limitation as to temperature range make them less convenient to use than other pyrometers. Mercury thermometers filled with nitrogen or carbon dioxide, to prevent boiling of the mercury, can be used to measure temperatures above 500°C. Such thermometers must be very carefully annealed at a temperature above the maximum to be recorded and allowed to cool slowly before the zero point, and therefore the readings, can be depended upon. The "zero-point" must be checked from time to time to note any change. The error at 500°C., in this way, may amount to as much as 20 per cent. of the change in the ice point.[1] A service thermometer, before being used, should be compared with two standard thermometers, which have been calibrated at a national laboratory. To do so, the thermometer and the two standards are placed in a bath of hot oil (completely immersed) and the readings taken. The correction which must be applied to the reading of the service thermometer, can be determined from the known temperature of the oil bath, as given by the two standard thermometers. The two standards are good as standards only so long as they check each other. If only the bulb is immersed, a correction equal to the temperature at one-half the height of the protruding column of mercury, as measured by a second thermometer, must be added to the reading. Both thermometers should be protected from direct radiation from the furnace.

Thermometers made of Jena glass and filled with a sodium-potassium alloy, which is liquid at room temperatures, have been used up to 700°C. (Baly and Chorley) and thermometers of quartz, using molten tin, have been used above 1000°C. (Dafour). More recently the latter instrument has been designed to read up to 1800°C. (Northrup).

Thermocouples.—The most common method of measuring temperature is by measuring the electromotive force developed by a thermocouple whose hot junction is at the temperature of the

[1] See *Bull*. Bureau of Standards, 1906, Vol. 2, No. 2, p. 189; also *Reprint* No. 32. Much useful information on mercurial thermometers is contained in this paper.

hot body. The couple is made by fusing or twisting together the free ends of two dissimilar wires. If the fused junction is at a different temperature from the two free ends of the wires, a difference in potential will be established between the hot ends and the cold ends of the wires, so that there will be an e.m.f. across the free ends of the couple equal to the algebraic sum of the difference in potential along the wires. By placing the junction, called the "hot junction," at the hot body so that it will be at the same temperature as the hot body, and by measuring the e.m.f. developed by the couple, we have a means of measuring
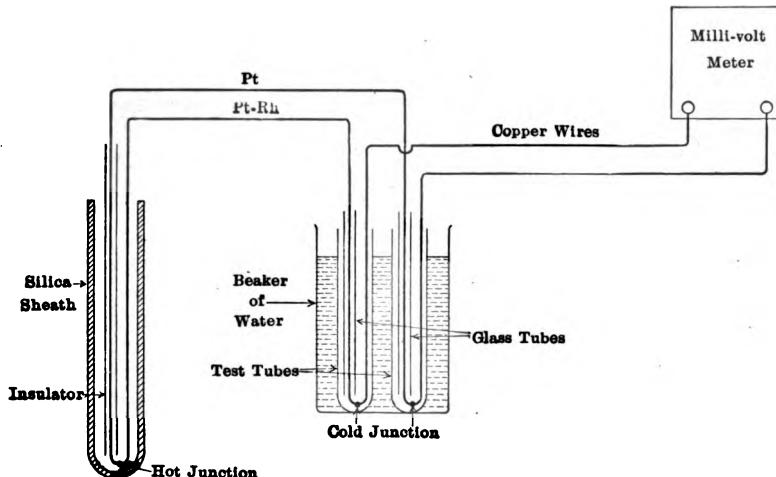
Fig. 62.—Thermo-electric method of measuring temperature.

the temperature of the hot body. The method of making the hot junction, whether by fusing or twisting the ends together, has no effect on the electromotive force developed by the couple, although oxidation, in the latter case, may introduce a large resistance which would affect the readings in case a deflection instrument is used to measure the e.m.f.

The best known of the thermocouples is the Le Chatelier couple which is made of wires of pure platinum and an alloy of platinum with 10 per cent. rhodium.[1] This couple is shown diagrammatically in Fig. 62. In this form with either fused

[1] This couple is quite generally called the platinum-rhodium couple. The couple using platinum with 10 per cent. iridium is now seldom used on account of the greater volatilization of the iridium which changes the readings of the couple.

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silica or porcelain casing and insulators it can be used to measure temperatures, intermittently, up to 1500°C. The deterioration of both couple and casing is very rapid at this temperature and it should not be used for any length of time above 1300°C. The outer casing is used to protect the couple from the direct action of the furnace gases or of the melt. The free ends of the couple wires are connected to copper leads, known as the cold junction, which lead to the millivoltmeter or other means of measuring the e.m.f.

The advantages of the Le Chatelier couple are its ability to resist high temperatures and oxidizing gases, its high melting point, and the constancy of its results which has been shown by Burgess to be very great. Its disadvantages are its first cost, comparatively low thermoelectric force, and its inability to withstand the action of certain metallic vapors and reducing gases.

In order to obtain the correct temperature of the hot junction from the electromotive force generated by the couple, it is necessary to observe the fundamental principles of the apparatus. The relationship between the temperature of the hot junction and the e.m.f., can be expressed by the formula

$$T = f(e) + \Delta t$$

where T is the temperature of the hot junction, e is the electromotive force of the thermocouple (in millivolts) on the basis of a cold junction temperature of 0°C., t is the temperature of the cold junction, and Δ is a constant which varies with both T and t. Δt is the cold junction correction and, in order to obtain the true temperature of the hot junction, it must be added to the temperature as computed from $f(e)$.

The relation between the e.m.f. and the temperature of the hot junction, assuming a cold junction temperature of 0°C., may be expressed by the formula $T = a + bE + cE^2$ where T is the temperature to be measured, a, b, and c are constants of the equation, and E is the e.m.f. This formula has been found to apply over the range from 300°C. to 1100°C. with an accuracy of 1°C. at 1000°C. Two other formulae which have been used are

$$E = a + b\theta + c\theta^2$$

and

$$\log E = a \log \theta + b$$

where E is the e.m.f., θ is the temperature of the hot junction, and

a, b, and *c* are constants. The latter formula applies over a very wide range of temperature and is especially useful for extrapolation above 1100°C. It is accurate to 1°C. at 1000°C.

The assumption is made in the above that the cold junction temperature is 0°C. If the cold junction is at some other temperature, although the couple was calibrated with a 0°C. cold junction, it is necessary to know what that temperature is and the value of Δ. Δ can be obtained from the following table with sufficient accuracy.

TABLE 4

Temperature, ° C.	Constant, Δ	Temperature, ° C.	Constant, Δ
0	1.00	800	0.54
100	0.89	900	0.52
200	0.76	1000	0.50
300	0.65	1100	0.49
400	0.61	1200	0.47
500	0.59	1300	0.46
600	0.57	1400	0.45
700	0.55		

The cold junction temperature is assumed to be room temperature.

The factors from 400°C. up are computed from the "preferred form" of cold junction correction according to FOOTE, "Note on Cold Junction Corrections for Thermocouples," *Bull.* Bureau of Standards, 1913, Vol. 9, p. 1. Also *Reprint* No. 202.

Before being put into use, the couple should be thoroughly annealed at about 1300 to 1400°C. This can be conveniently done by passing a current of about 14 amperes through it until the couple glows uniformly throughout its entire length. This operation is intended to eliminate parasite currents and make it immaterial which portion of the wire comes at the maximum temperature fall along the wire.

The platinum, or noble metal couples, are used in metallographic laboratories as pyrometric standards. These are the so-called "normal couples" which have been accurately calibrated either in the private laboratory or at one of the national laboratories, such as the Bureau of Standards at Washington or the National-Physical Laboratory at Teddington. The elements are usually one meter long and 0.6 mm. in diameter. These couples are supplied with certificates which give the values of the electromotive force in millivolts for each 100°C. from 300°C. to 1600°C.

The Bureau of Standards certifies the Le Chatelier couple for use at 1200°C. with an accuracy of ± 2°C. The cold junction temperature is usually made 0°C. but the Physikalisch-Technische Reichsanstalt, Charlottenburg, standardizes couples at 20°C., which is the average room temperature. The calibration curve is usually made from the data supplied by plotting the e.m.f.'s against the corresponding temperatures on rectangular coördinate paper. A smooth curve drawn through the points will give the correct temperatures for all values of the electromotive force.

Out of the demand for a couple which is less expensive than the Le Chatelier, and which has a higher thermoelectric force,[1] has come the development of the base metal couples using elements of nickel, iron, copper, and various alloys such as constantan, nichrome, etc. The high thermoelectric force of the base metal couple permits the use of millivolt meters of more solid construction, which in many cases is a particular advantage. These couples oxidize and become brittle and otherwise deteriorate much more readily than the Le Chatelier couple, and hence are limited to the lower temperatures. Kowalke has shown that pure metals and solid solutions give the most satisfactory results and are most constant, particularly if the structure is uniform.[2]

A rather special base metal couple, in that it can be used at comparatively high temperatures, is the Hoskins couple which is made of an alloy of nickel and 10 per cent. chromium, and nickel and 2 per cent. aluminum. This couple can be used, if need be, at temperatures exceeding 1200°C. if carefully protected from oxidation.

The high thermoelectric force of the base metal couples[3] makes them particularly useful in the measurement of the lower temperatures. The use of the copper-constantan couple has been advocated by the Geophysical Laboratory, Washington, as a precision instrument, particularly for the measurement of temperatures below 400°C. Its equation is given in the form

$$E = a\theta + b(1 - e^{c\theta}).$$

[1] The "thermoelectric force" of a couple is the change in e.m.f. per degree Centigrade and is used to compare the behavior of different couples.

[2] KOWALKE, "The Constancy of Base Metal Thermocouples as Related to Their Microstructure," *Trans.* Amer. Electrochem. Soc., 1914, Vol. 26, p. 199.

[3] The thermoelectric force of base metal couples is usually from 20 to 40 microvolts per degree Centigrade as compared to 10 microvolts per degree Centigrade for the Le Chatelier couple.

By dividing the interval between 0°C. and 900°C. into three parts, each interval can be expressed to a fraction of a degree by the formula

$$E = a + bt + ct^2.$$

The equation for the Hoskins couple has been found by the writer to be a straight line equation, at least within the limits of error of the ordinary measurement. This limit should certainly not be greater than 2 to 3°C. below 1000°C. The electromotive force of the couple, in this case, depends solely upon the difference in temperature between the hot and cold junctions, which is a decided convenience in routine work. If the electromotive force-temperature curve is not a straight line, due allowance must be made for the two junction temperatures. In laboratory practice it is usually convenient to calibrate and subsequently use the couple at normal room temperature of 20°C. Errors in applying the cold junction correction, if the temperature is slightly above or below 20°C., are bound to lie within the experimental error.

Various methods have been devised to eliminate the cold junction correction so that the temperature can be read without the necessity of correcting. These devices are not laboratory devices but are supplied by the makers of commercial pyrometers, from whom directions as to their use can be secured.

Thermocouples have been devised for use at temperatures above 1600°C. The materials used are principally carbon and graphite,[1] iridium and an iridium-ruthenium alloy, and tungsten and molybdenum.[2] The readings of these couples are apt to be erratic and more satisfactory determinations can usually be made by means of optical pyrometers.

The use of the thermocouple has been extended to the field of precision thermometry at the Geophysical Laboratory by employing multiple couples with twenty-five junctions.[3] Readings may then be made to 0.0001°C. for low temperatures. It is safe to say that only in exceptional cases is such high precision required in metallographical investigations, while the use of multiple couples offers certain disadvantages which are not common to calorimetric determinations.

[1] BIDWELL, *Phys. Rev.*, 1914, Vol. 3, Ser. 2, p. 450.
[2] NORTHRUP, *Met. Chem. Eng.*, 1913, Vol. 11, p. 45.
[3] See for example, W. P. WHITE, *Phys. Rev.*, 1910, Vol. 31, p. 135.

Measurement of the Electromotive Force.—The customary means of measuring the e.m.f. of a thermocouple, which is always but a few thousandths of a volt, or millivolts, is by means of a galvanometer or millivoltmeter. The galvanometers used with the base metal couples, which develop comparatively high e.m.f.'s, are of the pivot type. They are provided with scales which read either in millivolts, degrees Centigrade, or in degrees Fahrenheit. The resistance of the pivot type millivoltmeter is always comparatively low; on this account, changes in the resistance of the circuit can introduce appreciable errors in the readings. To minimize a change in resistance, the contacts should always be well made and the depth of immersion of the couple, or the length which is heated by the furnace, should be the same during calibration that it is during the subsequent use of the couple. The e.m.f. measured also varies with the resistance of the copper leads so that the same wires should always be used.

The lower thermoelectric force of the platinum couple requires the more sensitive suspended coil type millivoltmeter. On account of the more delicate suspension of the coil, these galvanometers can be made with resistances up to 500 ohms and still give sufficiently large deflections. This high resistance is sufficient practically to eliminate the error due to changes in the resistance of the circuit as just enumerated. The pointer can be set to read zero, or, if desired, it can be set to correspond to the cold junction. Burgess, in a discussion of galvanometer requirements for industrial and laboratory practice,[1] points out that the resistance must be sufficiently high for the couple with which it is to be used. "A galvanometer suitable for use with a Pt-PtRh couple may very properly be used with a low resistance base metal couple of higher e.m.f., by putting additional resistance into the circuit if necessary, but a galvanometer suitable for use with the base metal couple may be totally unfit for use with the Pt-Rh." He points out further that, even with the best pointer instruments, an accuracy of 5° is barely attainable with Pt-Rh couples and this only by paying attention to the numerous sources of error.

An improvement in the method of reading the deflections is secured by the use of a mirror galvanometer of the Deprez-d'Arsenval type and a telescope and scale. As Burgess points out,

[1] BURGESS and LE CHATELIER, "Measurement of High Temperatures," p. 134.

this results in a great increase in the sensitivity but not necessarily in the accuracy of the measurements.

A much more satisfactory method of measuring electromotive force is by means of a potentiometer. The principle of the potentiometric method of measuring electromotive forces can be made clear by means of Fig. 63, which represents the wiring of the Leeds and Northrup potentiometer indicator. The key *SC* is pressed down and the dry cell is balanced against the standard cell by means of the variable resistance *RR′* until the galvanometer shows a zero deflection. This establishes a drop in potential along the slide wire *DE* equal to the range of the in-
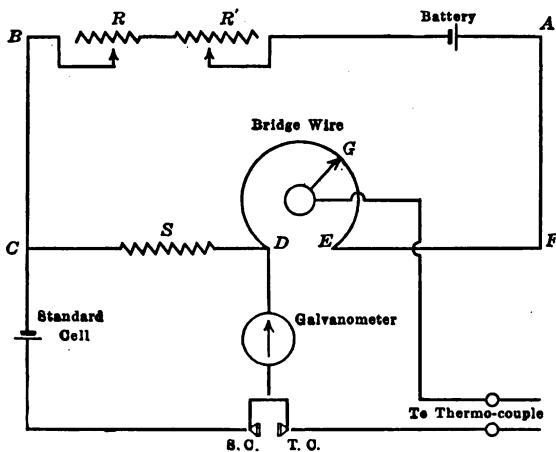
FIG. 63.—Wiring diagram of a potentiometer. (*Leeds and Northrup.*)

strument. To determine the e.m.f. of the thermocouple, the key *TC* is depressed and the position of the pointer *G*, on the slide wire, is varied until the galvanometer again shows a zero deflection. In this case the drop in potential along the slide wire is equal to and opposite to the e.m.f. of the thermocouple and can be read off the scale of the instrument.

It is the e.m.f. of the thermocouple which is measured, and not the current produced by that e.m.f. as in the case of the deflection instruments, so that this method has all the advantages of the null method as compared with the deflection method and the readings are independent of the resistance of the thermocouple circuit. In fact, the lead wires are frequently made of the same metals as the thermocouple wires (assuming base metals), so that the cold junction can be brought up to the potentiometer.

As a complete installation for work to 1°C., Dr. Burgess gives the following:

1. *A Standard Cell.*—The Weston normal unsaturated cadmium cell is generally used for this purpose. The portable cell has an e.m.f. at 20°C. of 1.0187 volts. The standard cell is used only to adjust the electromotive force between two points to the desired amount, between which, current is passed by an accumulator. A part of the latter e.m.f. is actually balanced against the thermal e.m.f.

2. *A Potentiometer.*—A potentiometer for work to 0.1°C. with a Pt-Rh couple must have a sensibility of one microvolt throughout the range of the instrument and a fairly low resistance. Contact, or thermal electromotive forces, must be eliminated as far as possible. By reading to one microvolt, the temperature at 1000°C. can be measured to about 0.1°C.

3. *A sensitive galvanometer* giving an appreciable deflection for ten microvolts. The usual type for this work is the Deprez-d'Arsonval galvanometer of small resistance.[1] If, instead of entirely compensating the thermal e.m.f., the last increment is determined from the galvanometer reading, the period should not be over five seconds. If readings are to be taken to 0.1°C., the galvanometer should have an appreciable deflection for one microvolt.

Of the potentiometers of the larger type which may be used in thermoelectric pyrometry may be mentioned the Leeds & Northrup, the Weston, the Cambridge, and the Wolff potentiometers, although there are numerous others which would doubtless satisfactorily serve the purpose. A "Potentiometer Indicator" which aims at combining simplicity with a fair degree of accuracy and still retain the potentiometric principle, is also made by Leeds & Northrup. Readings with this instrument can be made to about 3° C. with a platinum couple. A Weston standard cell is included in the equipment, so an accurate check of the dry cell circuit can be made at any time. The "Pyrovolter," as made by the Pyrolectric Instrument Company, also uses the potentiometric principle but does not contain a standard cell.

The Standardization of Thermocouples.—There are three principal methods of securing the calibration of a thermocouple:

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[1] The Leeds & Northrup type HN No. 2210, and the Weston Model 89 galvanometers have proven satisfactory for this work.

1. The standardization certificate can be obtained from one of the national laboratories on the payment of a small fee. The Bureau of Standards guarantees calibrations to two different accuracies, ± 2°C. and ± 5°C. at 1200°C. for the platinum couple. If the instrument used to measure the e.m.f. can be relied upon, it is sufficient to have the couple alone calibrated, but at times it is necessary to have the calibration made with the millivolt-meter connected to the thermocouple as it will be ultimately used, particularly if there is any temperature coefficient in the millivoltmeter.

2. It is obvious that if the e.m.f.'s corresponding to a number of hot junction temperatures are determined, the calibration curve can be plotted from the data thus obtained. It is not even necessary to go as far as this; for if a sufficient number of readings are obtained for the determination of the values of the constants in the equation of the couple, the calibration curve can be obtained by plotting the graph of the equation on rectangular coördinate paper, or by plotting the points them-selves and joining them by a smooth curve. Observations at three known temperatures are sufficient to give the accuracy required in these measurements. These points are generally secured by determining the e.m.f.'s corresponding to certain fixed points, usually the freezing points of pure metals or salts.

If the relationship may be represented by a logarithmic equation, the calibration curve can be obtained from one deter-mination. The e.m.f. corresponding to the freezing point of a pure metal, for instance copper, is determined and plotted on logarithmic paper. By drawing a straight line from this point to the temperature at which the e.m.f. will be equal to zero, *i.e.*, the cold junction temperature, the calibration curve is obtained. These values are generally transferred to rec-tangular coördinate paper to obtain the ordinary curve.

A number of fixed points which are used by the Bureau of Standards for calibrating pyrometers, are given in Table 5.[1]

Table 6 gives a convenient and inexpensive series which has been suggested by Burgess which requires the minimum precautions in manipulation but which gives an accuracy of ± 5°C.

[1] The metals tin, zinc, aluminum and copper may now be procured from the Bureau of Standards with certified chemical analyses and freezing points. Those interested should secure *Circular* No. 66.

TABLE 5.—FIXED POINTS

	Freezing points		Accuracy, °C.	Reproducibility, °C.
	°C.	°F.		
Tin...................	231.9	450	0.2	0.03
Cadmium.............	320.9	610	0.3	0.05
Lead................	327.4	620	0.3	0.05
Zinc.................	419.4	787	0.5	0.05
Antimony............	631	1,167	1.5	0.3
Sodium chloride......	800	1,472	2.0	1.0
Silver................	961	1,760	2.0	0.3
Gold................	1,063	1,945	3.0	0.5
Copper..............	1,083	1,980	3	1
Nickel..............	1,450	2,642	15	10
Palladium...........	1,550	2,822	15	5
Platinum............	1,755	3,191	20	10
Tungsten............	3,000	5,432	100	25
Carbon arc..........	3,500	6,332	150	50
Sun.................	6,000	10,832	500	100

TABLE 6.—FIXED POINTS

	Freezing points	
	°C.	°F.
Tin.......................................	232	450
Lead......................................	327	620
Zinc......................................	419	787
Aluminum.................................	657	1214
NaCl.....................................	800	1472
Cu.Cu$_2$O (eutectic).........................	1063	1945

3. The normal couple may be used to give an accurate reading of the temperature of the hot junction; that is, this reading may be used to replace the one obtained from the freezing point of a pure metal. To insure having the two hot junctions at the same temperature, they should be bound in metallic contact, or else placed in a small metal bar which is at the central portion of the furnace. Before taking a reading, the temperature of the furnace should remain constant for a short time. This eliminates any difference in the lag in the readings of the two couples. The reading of the furnace is determined by the thermocouple and the

electromotive force of the couple to be calibrated is noted. Two other similar determinations are made at sufficient intervals to cover the temperature range. The calibration curve of the couple is plotted from these three determinations. During calibration it is important to note the cold junction temperatures, and, under some circumstances, the depth of immersion, the millivoltmeter used, and any other points which might affect the readings.

The calibration of thermocouples by determinations at three known temperatures is sufficiently accurate up to 1200°C. but, at higher temperatures, the readings determined by extrapolation vary somewhat from the gas scale. The corrections which must be added to the readings as determined by the thermocouple are given in Table 7.

TABLE 7

| Thermocouple scale °C.	Correction °C.
300–1200	0
1300	+ 2
1400	+ 6
1500	+14

FOOTE; *loc. cit.*

Platinum Resistance Thermometers.[1]—It is well known that the electrical resistance of metals increases with the temperature. This is the principle which is used in platinum resistance thermometry and, inasmuch as electrical resistance can now be very accurately measured, a delicate means is afforded for measuring temperatures. The platinum resistance thermometer is shown in Fig. 64. The platinum coil is wound on a mica frame and is situated at the bottom part of the porcelain or silica tube in the "bulb." In measuring the resistance of the platinum wire, the error due to the heating of the lead wires must be eliminated. This may be done by means of the compensating leads shown in the diagram, or by measuring the potential across the platinum coil at the same time the resistance is measured. The current used is taken from a small cell which is usually contained in the temperature indicator. The strength of this current is necessarily small as any heat effect would introduce an error into the

[1] Platinum Resistance Thermometry has been very thoroughly discussed by WAIDNER and BURGESS, using their work at the Bureau of Standards as a basis; *Bull.* Bureau of Standards, 1910, Vol. 6, No. 2, p. 149. See also, *Reprint* No. 124, "Platinum Resistance Thermometry at High Temperatures."

measurements. The temperature range of this instrument is from −200°C. to about 1000°C.

In ordinary practice, resistances, or temperatures, are measured by means of a temperature indicator, of which there are two types, each using the principle of the Wheatstone bridge. In the Whipple Indicator the current passes through the platinum coil and a bridge wire which is wound on a large drum. By rotating the drum the resistance of the bridge may be varied to compensate the resistance of the bulb. When the galvanometer shows that there is no current across the bridge, the temperature in degrees Centigrade is taken off the drum scale. On account of the delicacy of the apparatus the scale is very open so that temperatures can be read to 0.1°C.

In the second type of temperature indicator a constant electromotive force is used. The resistances are adjusted to give a zero deflection of the galvanometer when the temperature of the bulb is 0°C. As the bulb temperature varies, the current across the bridge varies and in this way temperatures may be determined by deflections of the galvanometer.

In platinum resistance thermometry, it is of vital importance to have the instrument accurately calibrated. On the assumption that the resistance is proportional to the temperature,

Fig. 64—.Platinum resistance pyrometer. (*Burgess.*)

$$p_t = 100 \left(\frac{R_t - R_0}{R_{100} - R_0} \right)$$

in which p_t is the so-called "platinum temperature" according to Callender, and R_t, R_0, and R_{100} are the resistances at the temperatures $t°$, $0°$, and $100°$ respectively. $R_{100} - R_0$ is called the "fundamental interval" and $\dfrac{FI}{100 \, R_0}$ is called the "fundamental
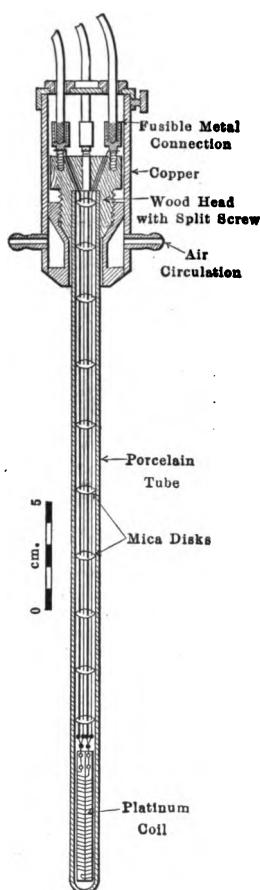
coefficient," c. In order to reduce the temperatures to degrees Centigrade, it is necessary to apply the following correction

$$d = T - p_t = \delta\left(\frac{t^2}{100^2} - \frac{t}{100}\right)$$

where δ is a constant which depends on the chemical composition of the platinum wire. Waidner and Burgess found δ to be 1.50 for the purest platinum and to increase to 1.80 for the less pure metal. δ and the other constants of the platinum thermometer were found to change somewhat with use, particularly if temperatures above 1000° were measured.

The value of δ is determined from observations at three known temperatures, usually 0°C., 100°C., and 444.7°C., the sulphur boiling point at 760 mm. A thermometer, calibrated at these temperatures, gives highly accurate readings up to 1000°C.

Radiation and Optical Pyrometers.[1]—Radiation from a hot body depends on the nature of that body and its temperature. We shall first consider the influence of the nature of the substance on the radiation.

Kirchoff has defined a "black body" as one which absorbs all the radiation falling upon it; *i.e.*, one whose reflecting and transmitting powers are nil. This conception is used as a standard in optical pyrometry and it is necessary to know how closely the hot body in question approaches the ideal black body. Substances such as carbon and the black iron oxide are regarded as "effectively" black bodies, while porcelain, platinum, etc., depart very appreciably from black bodies.

Kirchoff further pointed out that the radiation from within a chamber, the walls of which are at a uniform temperature, is the same as that of the ideal black body. Such a black body can be readily prepared in the laboratory by placing a block of carbon at the center of an electric tube furnace and stopping down the aperture of the tube by means of diaphragms to reduce drafts.

Black Body Temperatures. *Emissivity.*—Radiation from a black body is greater than that from any other substance; or, again, the more a given substance differs from a black body the less will be its radiation. Thus the radiation from a piece of carbon is many times that from a piece of platinum or magnesia at the same temperature. This difference in emissive power of dif-

[1] The laws of optical pyrometry and the most commonly used instruments have been very thoroughly discussed by WAIDNER and BURGESS, *Bull. Bureau of Standards*, 1905, Vol. 1, No. 2, p. 189. See also, *Reprint* No. 11.

ferent substances has given rise to the "black body temperature" of a substance, which is its temperature as determined by a radiation pyrometer which has been calibrated against a black body. The temperature of a body which is neither a back body nor the effectively black interior of a furnace, as measured by the radiation pyrometer, will have an apparent temperature which is lower than its true temperature. Or, if two substances are at the same black body temperature, their actual temperatures may vary considerably. Burgess states in this connection that if the black body temperatures of carbon and platinum are the same their actual temperatures will vary as much as 180°C. at 1500°C.

Intensity of Radiation vs. Temperature.—The Steffan-Boltzmann radiation law states that the radiation from a black body is proportional to the fourth power of the absolute temperature as expressed by

$$E = K(T - T_o)^4$$

where E is the total radiation from the hot body at $T°$ absolute to the surroundings at $T°_o$ absolute and K is a constant depending on the units used.

A question arises here, in view of what was just said on the relative emissive powers of various substances, as to the variation of the radiation of bodies other than black bodies, and how their true temperatures are to be obtained by the radiation method. As to the first part, it can only be said that the radiation of bodies other than black bodies increases more rapidly than the fourth power; or that the radiation approaches that of the black body with rise in temperature. Further, there is usually a definite relation between the black body temperature of a given substance and its actual temperature, so that if the emissivity of the substance in question is known, the temperature can be readily obtained.

The emissivities of a large number of metals have been determined with the micropyrometer by Burgess and Waltenberg.[1] The emissivity was calculated from Wien's relationship:

$$\log_{10} E = \frac{c \log e}{\lambda} \left(\frac{1}{T} - \frac{1}{S}\right)$$

where E is the emissivity for the wave length λ, $c = 14,450$, e is the Naperian base, and T and S are the true and equivalent or black body temperatures (absolute) of the substance. E for red

[1] *Scientific Paper* No. 242, Bureau of Standards, Oct. 24, 1914.

light where $\lambda = 0.65\mu$ was found to lie between 0.30 and 0.40 for a large number of metals (Pd, Pt, Ir, Rh, Ni, Co, Fe, Zr, Th, V, Cr, Mo, W) for both solid and liquid states. That for copper, silver and gold was found to be much lower, and for manganese, titanium and beryllium, much higher.

It is many times much easier to determine the black-body temperature of a metal than its true temperature. This is so particularly of wires and filaments, whose temperatures can be readily determined optically if the emissivity is known. These relationships have been determined by Mendenhall and Forsythe for tungsten, tantalum, molybdenum, and carbon filaments.

The methods of reducing black body temperatures to degrees Centigrade have been discussed by Burgess.[1]

The commonest method of measuring temperatures by means of these principles is by estimating the color to the naked eye. As the temperature of a body is raised above that necessary to produce visibility its color changes from red to white as shown in Table 8, which gives the approximate colors for iron and steel at various temperatures.

TABLE 8.—COLOR SCALE

	°C.	°F.
Dull red	500	930
Blood red	550	1020
Warm blood red	600	1110
Dark cherry red	650	1200
Cherry red	700	1290
Bright cherry red	800	1470
Light red	850	1560
Orange	900	1650
Lemon	1000	1830
Light yellow	1075	1970
White	1200	2190
Scintillating heat	1300	2370
Dazzling white	1500–1600	2730–2910

Different observers will see slightly different colors for the same temperature, but, if both are skilled, they will check very closely in estimating the temperature.[2] A severe cold or other temporary ailment can throw these results into considerable error.

[1] "Measurement of High Temperatures," p. 286.
[2] See McWilliams and Barnes, "General Foundry Practice."

The Féry Radiation Pyrometer.[1]—The Féry radiation pyro-
meter measures the total radiation from the hot body or funace
interior.　This instrument is illustrated in Fig. 65.　The radia-
tion from the hot body enters the large tube, which must be
carefully aimed in the direction from which the radiation comes
as heat waves.　This radiation is brought to a focus on the hot
junction of a copper-constantan thermocouple by the gold-plated
reflector, at the rear of the tube.　This radiation or heat creates
an electromotive force in the couple which is measured with a
sensitive millivoltmeter.　In no case does the actual hot junction
temperature exceed 80°C.

The focus varies with the distance from the hot body so that
it is necessary to refocus at each set-up.　The focusing is ac-
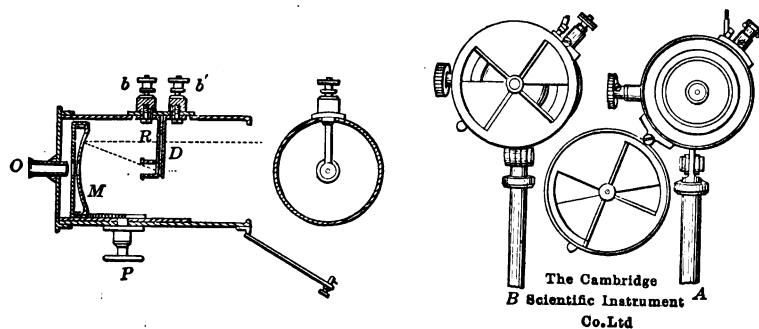
FIG. 65.—The Féry radiation pyrometer.

complished by sighting through the small telescope (0) on the
hot body, by means of the small rack and pinion movement,
until the image of the hot body is brought to a focus on the hot
junction of the thermocouple.

The scale of the millivoltmeter is usually provided with a
temperature scale so that temperatures can be read off direct.
It is to be noted from the Steffan-Boltzmann law that the ac-
curacy of the readings increases very rapidly with rise in tem-
perature, so that the radiation pyrometer becomes more and more
accurate over those ranges in temperature which are not readily

[1] A very excellent discussion of the pyrometers of this type has been given
by BURGESS and FOOTE, including an estimation of the errors which are
introduced in various ways.　*Bull.* Bureau of Standards, 1915, Vol. 12, p. 91.
Also *Scientific Paper* No. 250, "Characteristics of Radiation Pyrometers."

covered by the thermocouple. The Féry radiation pyrometer can be made recording, and some of the devices for this purpose will be discussed later.

There are two rules which must be observed in measuring temperature with the Féry radiation pyrometer:

1. The image of the hot body must overlap the hot junction.

2. The distance from the pyrometer to the hot body must be less than forty times the diameter of the hot body.

If the above rules are followed, moving the pyrometer closer to the hot body does not increase the amount of radiation falling on the hot junction and therefore does not affect its temperature. On the other hand, if the pyrometer is withdrawn to such a distance that the image formed is too small to cover the thermojunction, the readings obtained will be too low. Burgess and Foote have shown that not all Féry radiation pyrometers are constructed with a constant angular aperture,[1] so that the readings are not always independent of the focusing distance. The readings of these instruments are subject to considerable error when used at further distances than those used during calibration.

These pyrometers are usually calibrated against a black body so that the temperatures recorded are black body temperatures. To convert into actual temperatures, it is necessary to know the emissive power of the hot body. The temperature of a molten metal bath or of a furnace interior can be measured very readily by inserting a closed tube of porcelain or magnesia which acts as an effectively black body.

The Wanner Pyrometer.—The Wanner optical pyrometer measures temperature by measuring the intensity of the light of a certain wave length (monochromatic red or green) which comes from the hot body. The pyrometer as constructed by the Scientific Materials Company is shown in Fig. 66. It consists of two parts, one which forms a spectrum of the light which comes from the hot body, and one which selects a particular wave length and measures its intensity. Light from the hot body (in Fig. 66 the amyl acetate standard) comes through the opening (T_1) while light from a small incandescent lamp, which here serves as a photometric standard, comes through the opening (T_2). The prism (P_2) breaks up both rays into their spectra, which are brought to focus by the lenses (O_1) and (O_2) at (T_3).

[1] *Loc. cit.*

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The red hydrogen line ($\lambda = 0.653 \mu$) is selected from each of the two spectra by means of suitable diaphragms. The prism (P_3) polarizes the two beams of light in two directions perpendicular to each other so that in reality four spectra are formed at (T_3), only two of which, however, are used in the measurement. The two red rays pass through the analyzer (P_5) one ray illuminating the upper half and the other ray the lower half of the field of vision, usually so that a sharp line of demarcation separates the two halves. A rotation of the analyzer (P_5) causes one of the halves to increase, and the other half to decrease, in intensity so that they can be made equally bright, in which case the line separating the two halves disappears. The angle of rotation
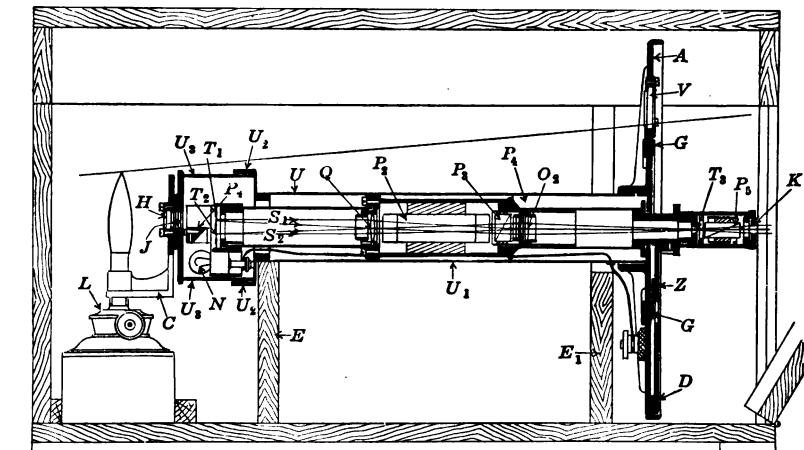

Fig. 66.—The Wanner pyrometer. *Scientific Materials Co.*

under these circumstances is used as a measure of the temperature of the hot body.

The intensity of the monochromatic radiation from the hot body increases very rapidly with the temperature. For black bodies this relationship is given by the Wien-Planck law, which may be stated as follows:

$$J = c_1\lambda^{-5} \cdot e^{\frac{-c_2}{\lambda T}}$$

where J is the black body intensity of radiation of the wave length λ, T is the absolute temperature, e is the base of the natural logarithms, and c_1 and c_2 are constants. All of the above quantities, except J and T can be determined, so that by measuring

J the value of T can be obtained and from T the temperature in degrees Centigrade.[1]

The logarithmic form of this equation is

$$\log J = C - \frac{c_2 \log e}{\lambda T}$$

that is, the log of the intensity is a linear function of the reciprocal of the absolute temperature. A similar equation can be written for another temperature (T_1) so that the ratio of the two intensities at two different temperatures (T) and (T_1) is given by

$$\log \frac{J}{J_1} = \log e \frac{c_2}{\lambda} \left\{ \frac{1}{T_1} - \frac{1}{T} \right\} = \log \frac{\cot^2 a_1}{\cot^2 a}$$

where the intensity is measured by means of a polarizing device, and a and a_1 are the corresponding deflections of the analyzer. From this it is clear that, if the intensity is known for some one temperature and wave length, any other temperature (above 650°C.) can be determined. The accuracy of the law has been demonstrated by Lumiére and Figerstein up to 2300°C., which justifies extrapolation, at least for black body radiation, up to the highest temperatures. For the higher temperatures, smoked glasses or other absorbing media are placed before the front glass to cut down the light.

Operation.—The telescope is sighted on the hot body and the analyzer is adjusted until the two halves of the field are of the same intensity. One value of the intensity is obtained automatically from the normal intensity of the light from the electric bulb, which is glowed by a definite and known current from a storage battery. The deflection of the analyzer, when set as described above, is a measure of the relative intensities of the monochromatic radiation from the hot body and the electric bulb and, therefore, gives the temperature direct. In practice two different currents are used, a weak one for low temperatures and a stronger one for high temperatures.

Calibration.—It is necessary from time to time to correct the readings of the scale. For this purpose a small amyl acetate lamp is provided as a standard. The telescope is sighted on the flame, which is set to burn at a standard height, and the analyzer is set at a reading corresponding to the known intensity of the

[1] Assuming the intensity J to be unity at 1000°C., according to this law it becomes 134 at 1500°C. and 2134 at 2000°C.

flame. This reading is the normal point as given by the makers. The lower half of the field is illuminated by the electric lamp and we will assume that the two halves are not of the same intensity. The resistance in series with the electric lamp is varied until the line of demarkation between the two halves disappears. The current flowing in amperes is noted and used in subsequent temperature measurements.

The failure on the part of the observer to bring the two halves of the field to exactly the same intensity is negligible. Assuming a mean error of 1 per cent. in the angle, the temperature at 1000°C. will be accurate to $\pm0.65°$, at 1500°C. to $\pm1°C$. and at 1800°C. to $\pm1.1°C$.

If the hot body is not an effectively black body, its emissivity must be known in order to convert black body temperatures into degrees Centigrade. As the emissivity of many such bodies is known, it is usually possible to secure an "open scale" with the instrument so that temperatures of bodies with that emissivity can be read off direct.

The Morse Thermogauge or Holborn-Kurlbaum Pyrometer. The Morse Thermogauge or Holborn-Kurlbaum[1] optical pyrometer measures temperature by matching the intensity of monochromatic red radiation of a filament with that from the hot body. The current in amperes which is required to produce this in the filament is then converted into degrees Centigrade.

The apparatus is shown in Fig. 67 and consists of an accumulator, or other source of electrical energy, a milliampere meter to measure the current, a telescope tube which contains a small horse-shoe filament at the focal plane of the objective, and a resistance in series with the filament and the milliampere meter. When the telescope is sighted and focused on the hot body, the filament is superposed on the image of the hot body. If the filament is at a lower temperature than the hot body, it appears as a dark line on a light background, while, conversely, if it is at a higher temperature, it appears as a light line on a dark background. The resistance in series with the filament is varied until the filament just disappears in the image of the hot body, when the corresponding reading in milliamperes gives the temperature.

The lower limit of this pyrometer is about 600°C. (1110°F.), at which temperature the radiation is nearly all monochromatic

[1] Preuss, Akad. Wiss. Berlin Sitz. Ber., 1901, Vol. 30, p. 712. This pyrometer is made in this country by Leeds & Northrup.

red. This is true up to nearly 800°C. so that in this temperature range monochromatic radiation is secured without the use of light filters. Above 800°C. one or more red filters are placed in front of the eyepiece in order to obtain monochromatic red for matching the intensities. When used for temperatures above 1500°C. overheating the filament is prevented by cutting down the radiation from the furnace either with a red glass or a double prism reflector.
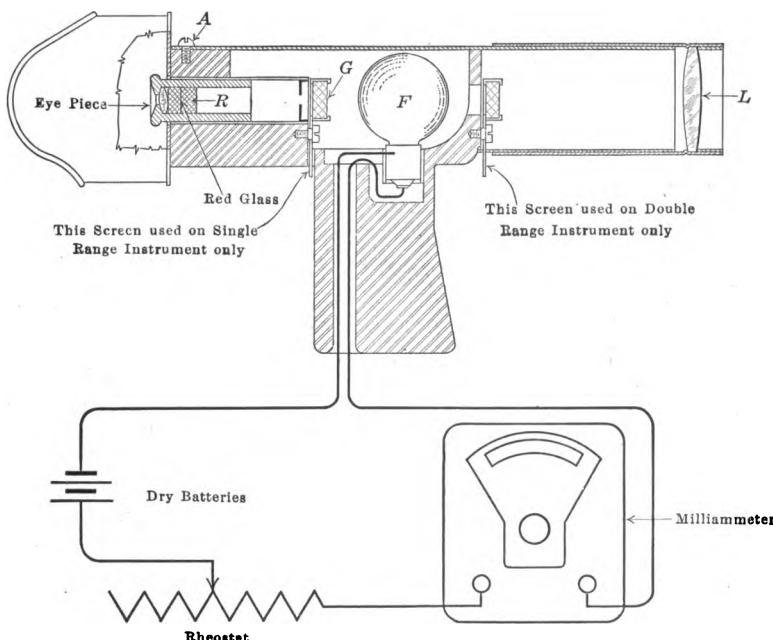

Fig. 67.—The Leeds and Northrup optical pyrometer.

The necessity of using color filters producing practically monochromatic radiation has been pointed out by von Pirani.[1] The "effective wave length" of the color screen and the correct means of extrapolation to secure correct readings at the higher temperatures, have been dealt with by Hyde, Cady and Forsythe,[2] and by Foote of the Bureau of Standards.[3]

In spite of the empirical principle of this method, the accuracy of the readings, as shown by Burgess, is all that can be desired.

[1] *Verh. deuts. phys. Gesell.*, 1913, Vol. 15, p. 836; 1915, Vol. 17, p. 47.
[2] *Phys. Rev.*, 1915, Vol. 6, p. 70.
[3] *Scientific Paper*, No. 260, March 13, 1916.

At 700°C. the average of five readings check a thermocouple to ±1.5°C., and at 1350°C. to ±1°C.

Calibration and Ageing the Filament.—A new filament, before being used, should be aged by heating to about 1600°C. for at least twenty hours, after which the readings remain constant for temperatures under 1500°C. The instrument is calibrated by making determinations at three known temperatures covering the range. These readings are then plotted on coördinate paper and a smooth curve drawn through the points. This curve is the calibration curve for the filament used. The coördinates of this curve are temperatures in degrees Centigrade or Fahrenheit and milliamperes. A formula of the form

$$M.A. = a + bt + ct^2$$

can also be used either for intrapolation or for plotting the curve, but this is hardly necessary.

There are other handy and efficient optical pyrometers on the market, among which may be mentioned the Féry Absorption Pyrometer, and the Shore Pyroscope, but it will hardly be necessary to describe them in detail.

Seger cones and sentinel pyrometers are seldom used in the metallographic laboratory to measure temperatures.

Of the uses which are made of pyrometric determinations, with the exception of thermal analysis, it may be said that they are principally for measuring temperatures during melting and pouring operations and during heat treatment. In the former case the optical pyrometer is generally to be preferred because the requisite degree of accuracy can be obtained and without disturbing or contaminating the melt. It should be remembered that, unless the instrument is specially calibrated, the temperatures recorded are black-body temperatures and that it may be necessary to correct for the emissivity of the objects whose temperature is desired. Temperature measurements during heat treatment are generally made pyrometrically. The thermocouple is placed within the furnace, through a hole in the wall or in the door. The couple should always be protected by means of an outer casing to avoid deterioration of the couple wires. Unless the readings are independent of the resistance of the circuit, the "depth of immersion" should be kept constant. The hot junction should always be close to the specimens being treated and is generally placed within a block of steel in order

more closely to simulate the temperature conditions within the specimens.

Thermal Analysis.—We come now to the one most important use which is made of pyrometry in the metallographic laboratory. Thermal analysis, along with the microscopical investigations, offers the simplest and most direct means of establishing constitution diagrams so that considerable emphasis is placed both on the methods employed and on the interpretation of the results. In the following we shall see how it is that melting points, transformation points and the like are determined and how, by the interpretation of the results, even the nature of the transformations can be established, at least within certain limits.

The fundamental reason why it is that thermal analysis is applicable in this field is because it indicates the temperature, or temperature interval, at which the "heat effect," accompanying the constitutional change, takes place. A "heat effect" is the direct result of a sudden change in the total heat (energy) of a metal or alloy, such as the absorption or evolution of the latent heat of fusion during melting or freezing. From the principle of thermo-dynamics that high temperature modifications must necessarily have the greater amount of heat or energy, it follows that the heat effect is always an evolution of heat on cooling and an absorption of heat on heating. Therefore, the heat effect causes a retardation in the fall or rise in temperature during the change, the aim of thermal analysis being to locate the temperature, or temperature interval, at which the heat effect takes place and to give evidence of the nature of the heat effect.

By means of the methods of thermal analysis the temperature of the alloy, when heating up or cooling down, is followed. The data obtained are plotted as heating or cooling curves, which, according to the method used, are known as time-temperature curves, inverse-rate curves, direct-rate curves, differential curves, and derived differential curves.[1] These curves show the temperatures at which the retardations take place, and therefore the temperatures at which the changes take place.

The Time-temperature Curve.—The time-temperature curve is obtained by reading the temperature, as measured with a ther-

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[1] A more appropriate name for the differential curve would be "difference curve," as suggested by Desch, but the more customary name will be used here.

mocouple, from time to time, and by plotting the temperature against the time on coördinate paper. A cooling curve of this type is shown in Fig. 68 which is a typical curve obtained for the cooling and solidification of a pure metal. The branch *A–B* corresponds to the cooling of the melt and the branch *C–D* to the cooling of the solid, while the branch *B–C*, the time interval over which the temperature remains constant, corresponds to the solidification of the melt. The exact shape of the branches *A–B* and *C–D* depends upon the conditions under which the metal is cooling but is of no great importance here. The chief point is, that, as soon as the melt commences to freeze, the temperature halts and remains constant as long as there is any melt left.[1]
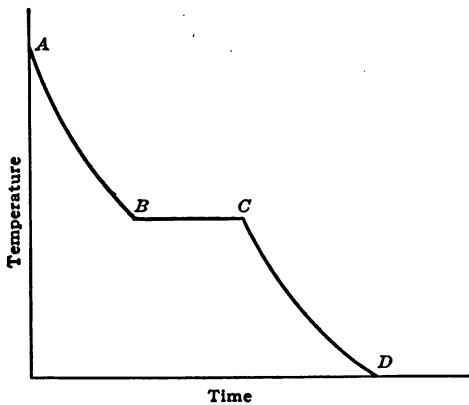

FIG. 68.—Time-temperature cooling curve.

As a rule, the intersections at *B* and *C*, especially at *C*, are smoother than is shown in Fig. 68. This is usually due to the solid deposited on the pyrometer which is cooled slightly lower than the remaining melt by the conduction of heat along the couple. This rounding off commences as soon as the supply of heat from the solidifying melt is less than the conduction along the thermocouple.

The principal use which is made of this method is to determine freezing or melting points of pure metals and of eutectics. Conversely, the method is also used to check the thermocouple readings against the known temperatures at the freezing points of pure metals. It happens many times that the melt supercools

[1] We know from the phase rule that the temperature remains constant in a one-component system as long as two stable phases, here solid and melt, co-exist.

to some extent, as is shown in Fig. 69 for pure tin. This effect and the rounding of the transition at *C*, Fig. 68, must be eliminated in the determinations by using sufficient metal to give a
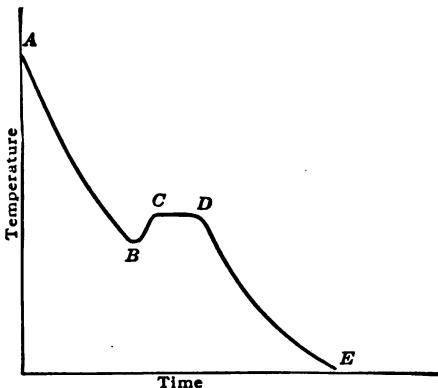

FIG. 69.—Supercooling shown by a cooling curve.

horizontal line at the solid-melt equilibrium. Many of the heat effects which occur during transformations in the solid state are too small to be brought out by this method of obtaining cooling curves.

The Inverse-rate Curve.[1]—The data for the inverse-rate curve are obtained by measuring the length of time, Δt, required by the specimen to pass through successive and constant intervals of temperature, $\Delta \theta$. By plotting $\Delta t/\Delta \theta$ (or simply, Δt) against θ, a cooling curve of the type shown in Fig. 70 is obtained. As long as the change in temperature is uniform, there is no abrupt change in Δt. As soon as there is a retardation in the rate of heating or cooling, the time interval Δt becomes correspondingly larger. This accounts for the sharp


FIG. 70.—Inverse rate cooling curve.

break at the point *B* and the cusp *C*. The temperature of the heat effect is not shown by any particular point, such as *B* or *C*,

[1] First used by Osmond. See *Memoirs* de l'Artillerie Marine, 1887, Vol. 12, p. 573; and also *Journ.* Iron & Steel Inst. 1890, No. 1, p. 38.

which are arbitrarily chosen, but can be at any temperature
intermediate between the first break and the cusp. For this
reason the actual temperature of the freezing point should be
read off and noted. The cold junction temperature is gener-
ally noted at the same moment. By decreasing the interval
of temperature, $\Delta\theta$, the break at B will more closely coincide
with the true temperature of the heat effect, but Burgess has
shown that nothing is gained by decreasing it to less than 2°C.
As soon as the melt has entirely solidified (a point which likewise
is not represented on this curve) there is a comparative ac-
celeration in the rate of cooling. This causes the sharp return
from the cusp as shown on the curve. The metal then resumes
its normal rate of cooling for the solid state under the existing
conditions. Under no circumstances can the values of Δt
become zero or negative.

This method of recording heating and cooling curves has
been used very extensively and is the one which gives greatest
satisfaction for determining the ranges of solidification of a
series of alloys. It is also used to determine changes in the
solid state, although for this work
good results depend on having some-
what exceptional facilities for deter-
mining the intervals of time (large
potentiometer.)

Intervals of Temperature- $\Delta\theta$
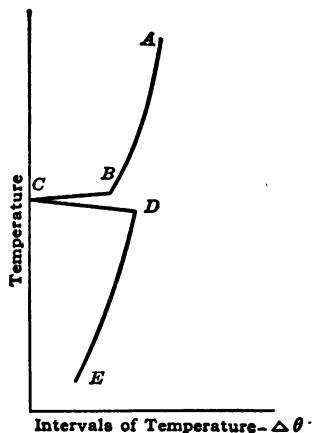
FIG. 71.—Direct rate cooling
curve.

The Direct-rate Curve.—Data
for the direct-rate curve are ob-
tained by measuring the drop in
temperature, $\Delta\theta$, for a constant
increment of time, Δt. By plotting
$\Delta\theta$ against θ the direct-rate curve
is obtained which gives the rate of
heating or cooling at any temper-
ature. At the freezing point the
rate of cooling is zero and the curve
intersects the zero time axis as shown
in Fig. 71. This method, while giv-
ing very satisfactory results, has not proven as popular as the
inverse-rate method.

The Differential Curve.—It was early recognized that external
influences had a considerable effect in causing irregularities on
the cooling curves. To eliminate errors of this kind and to

render the results relatively independent of variations in the rate of heating or cooling, Roberts-Austen devised the method of thermal analysis now known as the "differential" method. This was accomplished by placing a neutral body in the furnace, one which would heat up or cool down under the same conditions as the test specimen but which would produce no heat effect. By measuring the difference in temperature between the test specimen and the neutral body, it was possible to note any heat effect in the test specimen by the sudden change in the difference in temperature, which would invariably accompany such a heat effect. To accomplish this a double thermocouple with two hot junctions was devised, which is now called a "differential couple." At present it is made by connecting two pieces of platinum wire by a short piece of platinum-iridium, wire forming two hot junctions. One of the junctions is placed in the test

Fig. 72.—Differential cooling curve.

specimen and the other in the neutral body. As long as the test specimen and the neutral body are the same temperature, the potentials generated by these two couples will be equal and opposite; therefore, the galvanometer will show a zero deflection. In practice the deflection of the galvanometer will vary slowly but uniformly with rise or fall in temperature, due to slight differences in the rates of heating of the test specimen and the neutral body, but as soon as the test specimen passes through a transformation, the change in the deflection will be quite rapid. It is possible to use a very sensitive galvanometer to measure differences in temperature, so that heat effects can be followed with great accuracy. The temperature of the test specimen is measured at all times with a second thermocouple.

The differential cooling curve is obtained by plotting differences in temperature, expressed in millivolts ($\theta - \theta'$), and the temperature (θ) as shown in Fig. 72. At B the test specimen evolves a certain amount of heat and the difference in temperature increases to C. The temperature corresponding to the point B
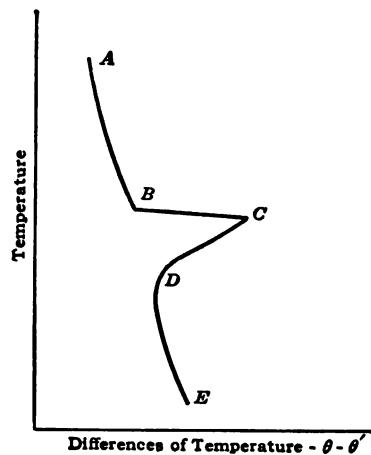
gives the temperature at which the heat effect begins. The return of the curve from C is rather gradual, as is shown in the figure.

Platinum, porcelain, and nickel are very commonly used as neutral bodies in thermal analysis The size of the neutral body should be such that, except during the heat effect, it will heat up or cool down at practically the same rate as the test specimen. An arrangement for holding the test specimen and the neutral body (25 per cent. nickel steel), which is used in the writer's laboratory, is shown in Fig. 73. The point in mind is that the two bodies should be placed symmetrically in the holder, which also serves as a temperature equalizer, and that each should receive an equal supply of heat.


A = Temperature Couple
B = Differential Couple
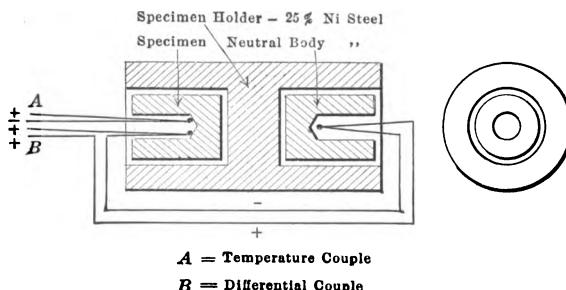
Fig. 72.—Specimen holder for differential curves.

The Derived-differential Curve.—Rosenhain suggested plotting the change in the difference of temperature $\Delta(\theta - \theta')$ for a constant interval of temperature, $\Delta\theta$, against the temperature.[1] This curve, known as the "derived differential," brings out the heat effect more sharply than the differential curve and is now a very popular method of plotting the above results. An example is shown in Fig. 76. The leading characteristic of this curve is the sharp return from the cusp, which gives an exaggerated prominence to the heat effect. This is due to the fact that the function $\dfrac{\Delta(\theta - \theta')}{\Delta\theta}$ changes sign at the peak of the differential curve and gives negative values for the derived differential curve, whereas the values of $\theta - \theta'$ on the differential curve remain positive at this point. It was noted above that the inverse-rate curve also has a sharp return from the cusp but that

[1] *Proc.* Phys. Soc., 1908, Vol. 21, p. 180.

Δt must always have a positive sign, while $\Delta(\theta - \theta')$ can and usually does have negative values. According to this, the inverse-rate curve and the derived-differential, while being very similar in practice, are not exactly alike.

Guertler's Modification of the Differential Method.[1]—Guertler has suggested a modification of the differential method, as a means of determining the effect of slight variations in composition on a transformation point. For example, if the effect of nickel on the transformation of iron is to be determined, a sample of pure iron would be used in place of the neutral body. If the transformation on cooling takes place first in the pure iron, the deflection of the differential millivoltmeter will be, let us say, positive. On the other hand, if nickel raises the transformation point, the heat effect will take place in the alloy before it will in the pure metal, and the deflection will be of the opposite sign, or negative. The chief advantage of this method is that the determination is made independent of the usual error in pyrometric measurements, as it is the direction of the first deflection and not the temperature at which it occurs which gives the desired information. Therefore, this method is especially useful when small additions of the second metal are under consideration.[2]

The use of the differential method is limited, at present, to locating transformations in the solid state. In this it is particularly useful, as it can be made highly sensitive without resorting to any but the simpler apparatus. In fact, it has been the author's experience that, in ordinary work, it is the most sensitive and accurate method of thermal analysis as yet developed, although Burgess and Crowe have shown that by using a special set-up, to be mentioned later, the inverse-rate curve can be made equally as sensitive.

The differential method is to be chosen in preference to the inverse-rate method because the measurement of differences of temperature can be made more sensitive and accurate than the measurement of intervals of time. This is so, because an error in estimating the exact moment to take the reading directly affects the reading in the latter case while it does not so much in the former, while minor variations in the rate of temperature

[1] Substantially as given in Dr. Guertler's lectures at the Royal School of Technology, Charlottenburg.

[2] This method can be carried out very readily with the holder shown in Fig. 73.

change produce no such sudden deflection on the differential curve as on the inverse-rate curve.

Apparatus Used in Thermal Analysis.—The electric tube furnace is the one most commonly used in thermal analysis. It is convenient, gives good heat insulation and can be heated up or cooled down at fairly uniform rates. The porcelain tube must be protected from the metal of the specimens and the thermocouple. This can be easily accomplished when setting up the apparatus and requires no special discussion. To prevent oxidation it is best to evacuate the chamber or to pass an inert gas through but many times it is sufficient to pack lump charcoal about the specimen and stop up the ends of the tube with asbestos wool.

Various experimenters have attempted to increase the uniformity of heating and cooling. Burgess has used an electric tube furnace which is made free from lag by eliminating the magnesia insulation of the ordinary tube furnace. The supply of current is kept constant by using a storage battery as a source, and the resistance is varied at a uniform rate by means of a water rheostat.

Rosenhain has used a fairly long tube furnace which is wound to give a uniform temperature gradient from one to the other.[1] The temperature range corresponds roughly to the temperature range of the heating or cooling curve. By raising or lowering the specimen within the furnace at constant rate, uniform heating or cooling can be obtained. Scott, at the Bureau of Standards, has used a modification of the Rosenhain furnace and apparently with great satisfaction. A description of this furnace has just appeared.[2] Either of these furnaces permits the use of a vacuum or a reducing atmosphere.

The thermocouple is the almost universal method of measuring temperature in thermal analysis. The couple should be placed in the specimen in a manner to permit the best possible flow of heat from the specimen to the hot junction.[3] The potentiometer (large type) with mirror galvanometer is used in all accurate thermal analysis on account of its greater sensitivity and accuracy, as compared with the ordinary millivoltmeter and because the exact moment for taking the readings can be more

[1] *Journ.* Inst. Met., 1915, No. 1, p. 164.

[2] Scott and Freeman Scientific Paper No. 348, Bureau of Standards.

[3] The question of lag has been dealt with by HAYES, *Proc.* Am. Acad. Arts and Sciences, 1911–12, Vol. 47, p. 1.

closely determined. The small potentiometer of Leeds and Northup and the suspended coil millivoltmeter of Siemens and Halske (high resistance) are also quite generally employed in this work.

Time, or intervals of time, are measured by means of a chronograph or else a stop watch or a pair of stop watches, used alternately. One of the commonest types of chronograph used is the drum chronograph which rotates at a very uniform rate. A line is traced out on the drum with a pen. At the moment of the reading, a key is depressed and the pen is deflected by an electromagnet. In this way, distances between deflections give time intervals. The reel type chronograph is used to some extent in this work but it is not constructed at present to give the accuracy of the drum or astronomical type. Rosenhain has described a drum chronograph which traces out the inverse-rate curve and so eliminates the necessity of transferring the record of the curve from the drum to the coördinate paper.[1]

As an example of an extra-refined equipment for use in obtaining inverse-rate and differential curves may be taken the following, as used at the Bureau of Standards.[2] The furnace was made with a minimum of mass to avoid lag in heating and cooling and was heated by alternating current from a motor-generator which received its current from a storage battery. The current was automatically increased or decreased by means of a salt water rheostat to produce a uniform temperature gradient. The furnace was evacuated at all times with a two cylinder Geryk pump, which, with drying tubes of phosphorus pentoxide, maintained the pressure as low as 0.01 mm. Hg.

Temperature was measured with Pt–PtRh couples carefully calibrated and checked from time to time. Contact with the iron produced no appreciable change in the readings. Differences in temperature were measured with a Pt–PtIr–Pt differential couple. Temperature e.m.f.'s were measured with a large Wolff (Diesselhorst) potentiometer of low resistance using a Leeds and Northrup moving coil galvanometer which gave, when critically damped, a deflection of 25 mm. at 2 meters for 20 microvolts. Every time the zero scale reading crossed the cross hair of the reading telescope, the time was noted by pressing the key of the

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[1] *Loc. cit.*

[2] Burgess and Crowe, *Bull.* Bureau of Standards 1914, Vol. 10, p. 315; also, *Scientific Paper*, No. 213.

chronograph (motor driven Geneva chronograph). Distances between successive deflections were taken as intervals of time. These corresponded to *ca.* 2°C. temperature intervals for the inverse-rate curves. Times were corrected by means of the Bureau's standard clock which was located in a constant-temperature room and were obtained to 0.1 second.

Differences in temperature for the differential curve were read with a Siemens & Halske moving coil galvanometer of 200 ohms
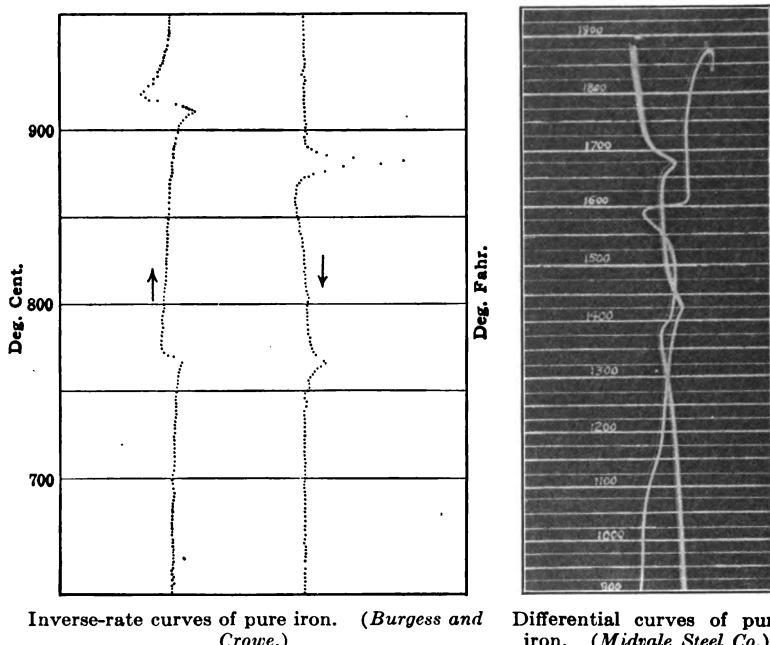
Inverse-rate curves of pure iron.   (*Burgess and Crowe.*)

Differential curves of pure iron.   (*Midvale Steel Co.*)

Fig. 74.

resistance.   The readings were sensitive to nearly .01°C. which was sufficient.

Two of the curves obtained in this way are reproduced in Fig. 74.

Autographic and Photographic Recording Devices have been used for obtaining heating and cooling curves. The autographic recording devices are made in various forms, consisting principally of a millivoltmeter (for measuring θ), a chronograph which actuates a band or disc of paper at a uniform rate (for measuring t), and a mechanism which causes the pointer of the

millivoltmeter to draw the curve on the paper. As the coördinates of the points on the curve are time and temperature, the curve traced will be the ordinary time-temperature curve. Among these autographic recording devices may be mentioned the Thread Recorder made by the Scientific Instrument Company, and the Hoskins, Bristol, Brown and Thwing Recording Pyrometers. The latter four mentioned are intended primarily for use with base metal couples which develop high e.m.f.'s. Leeds and Northup have developed a recording potentiometer and an instrument for recording differential curves using two galvanometers.

The first photographic recording device was the apparatus of Roberts-Austen.[1] A beam of light was reflected by means of a mirror on to the mirror of a suspended coil galvanometer, from which it was in turn projected on to a photographic plate. The plate was moved in a vertical direction at a uniform and constant rate to make its displacement proportional to the time. The curve traced by the spot of light was the time-temperature curve. Other similar devices have been constructed but they operate on essentially the same principle.

The Le Chatelier-Broniewski apparatus is a modification of the Saladin photographic recording device, with which either the time-temperature curve or the differential curve can be secured. Fig. 75 shows diagrammatically the arrangement of this apparatus for recording the differential curve. A Nernest lamp projects a beam of light on to the mirror of the differential galvanometer, (*A*). The deflection of the beam of light is proportional to the difference in temperature. The beam from (*A*) is projected through the Saladin prism (*C*) which converts the deflections from a horizontal plane to a vertical plane. On the photographic plate, therefore, difference in temperature is represented by vertical distances. The beam, on emerging from the prism (*C*) falls on the mirror of the galvanometer (*B*) which is connected to the thermocouple in the test specimen. Horizontal deflections of this mirror correspond to temperature. The resultant curve, as traced on the photographic plate, is the differential curve. Curves obtained with this apparatus are given in Fig. 74 at the right.

The time-temperature curve can be recorded with this appa-

[1] *Proc.* Roy. Soc., 1891, Vol. 49, p. 347; also "First Report Alloys Research Committee," *Proc.* Inst. Mech. Eng., 1891, p. 543.

11

ratus by using a chronograph in place of the differential galvanometer. The beam of light, on passing through the apparatus, is deflected vertically in proportion to the time, and horizontally in proportion to the temperature of the test specimen. The curve traced on the plate is the time-temperature curve.[1]

In order to compare the inverse-rate and differential curves, both of these curves were recorded simultaneously with instruments in the author's laboratory, first with the Leeds and Northrup potentiometer indicator and then with the Weston large model potentiometer. Time intervals were measured with a stop watch.


A = Differential Galvanometer

B = Temperature Galvanometer

C = Saladin Prisim

D = Photographic Plate
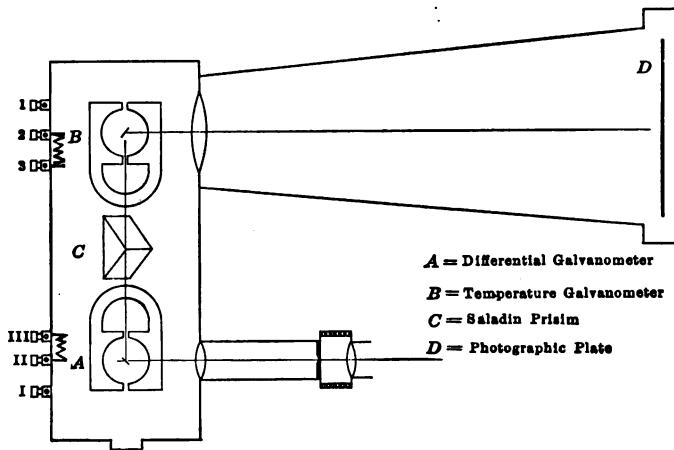
Fig. 75.—Le Chatelier Broiniewski apparatus. (*Pellin, Paris.*)

The curves obtained are shown plotted in Fig. 76. The two inverse-rate curves show that the large potentiometer, by giving very precisely the moment for taking the reading, gives a smoother curve. It may also be noted that the same difference is not apparent on comparing the differential curves. It seems obvious that differential curves require decidedly less pretentious apparatus than inverse-rate curves do, to give about the same degree of accuracy.

Thermal Analysis. *Pure Metals.*—The heating and cooling curves of pure metals have already been given above. (See Fig. 68.)   The temperature corresponding to the horizonal *B–C*

[1] For a novel method of obtaining direct-rate curves with an induction galvanometer and the Le Chatelier-Broniewski apparatus, see DEJEAN, *Rev. de Met.* 1905, Vol. 2, p. 701; 1906, Vol. 3, p. 149.

is taken as the freezing point. This is usually well defined so that little difficulty is experienced in determining the proper temperature. It is important, in this connection, to use a sufficient quantity of metal in order that there shall be no doubt as to the location and character of the heat effect. In the larger laboratories melts weighing from 100 to 300 grams are commonly used. Smaller amounts may be used, but if so, the wall of the thermocouple casing should be made as thin as possible. If the melt is subject to supercooling, it may be advantageous to inoculate at the freezing point with small chips of solid metal
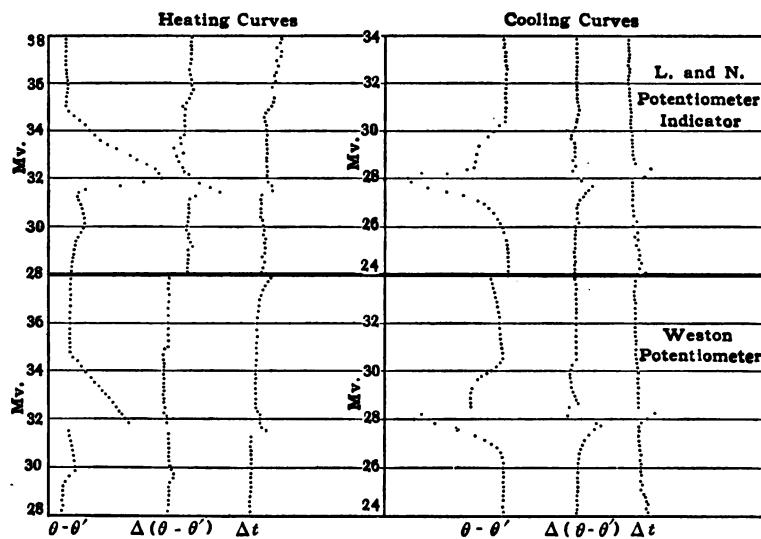

Fig. 76.—Heating and cooling curves of medium-carbon steel. Comparison of inverse-rate and differential curves; comparison of recording instruments.

and to stir with a stirring rod. It is much better to allow the melt to cool down with as little disturbance as possible. Cooling curves of pure zinc, silver, copper, etc., are used in the calibration of thermocouples.

Allotropic transformations in pure metals give curves of the same type as the above. The latent heat of transformation is somewhat less than the latent heat of fusion so that the heat effect may be much smaller, even so small as to fail to indicate a heat effect on the curve. For this reason it is often necessary to employ the refinements discussed above to obtain the exact transformation temperature.

Binary Alloys.—From what has already been said it is quite clear that inasmuch as alloys give off their latent heat of fusion on solidifying, thermal analysis can be employed to determine the solidification intervals. It has been possible to go further and correlate, at least in a general way, the shape of the cooling curve and the genesis of the alloy. On this account the thermal evidence is used as the basis of the construction of the diagrams, bearing in mind the relationships shown in the following. If, for any reason, the thermal evidence is not clear or conclusive, the results should be checked by microscopical analysis and other means.

Type I. *Solid Solutions.*—The cooling curve of a solid solution is shown in Fig. 77a. The branch B–C corresponds, as before,
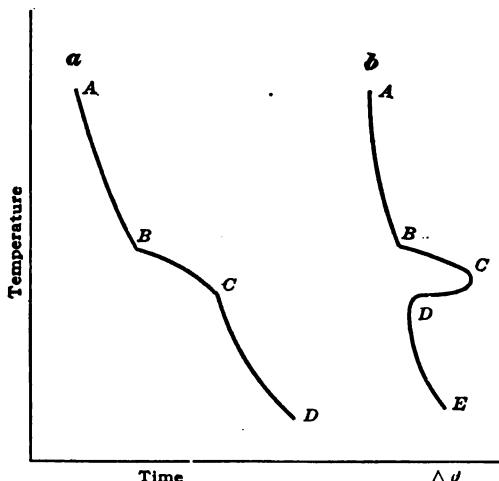

FIG. 77.—Cooling curves of a solid solution: a, time-temperature and b, inverse-rate.

to the solidification of the melt. The solid commences to form at about the point B and continues to form as the temperature drops from B to C. At C the entire mass has solidified. The point B is a point on the liquidus and the point C, theoretically, is a point on the solidus. In practice it is not possible to determine the solidus by means of cooling curves, as the transition from the branch B–C to C–D is so smooth that the estimation of the exact temperature is impossible. The cooling curve of the same alloy taken by the inverse-rate method, is shown at b in Fig. 77. The cusp is somewhat more rounded than that for

pure metals and the temperature interval is somewhat greater, corresponding roughly to the range of solidification. The cooling curve of a binary alloy of this type, corresponding to the minimum of Type *I-b*, is the same as that of a pure metal because the temperature remains constant during solidification.

Type II. *Eutectiferous Series.*—The cooling curves of an eutectiferous series are shown in Fig. 78. The cooling curves of the pure metals *A* and *B*, and of the solid solutions *α* and *β*, are the same as those already discussed under their respective headings. The cooling curve of the eutectic is the same as that
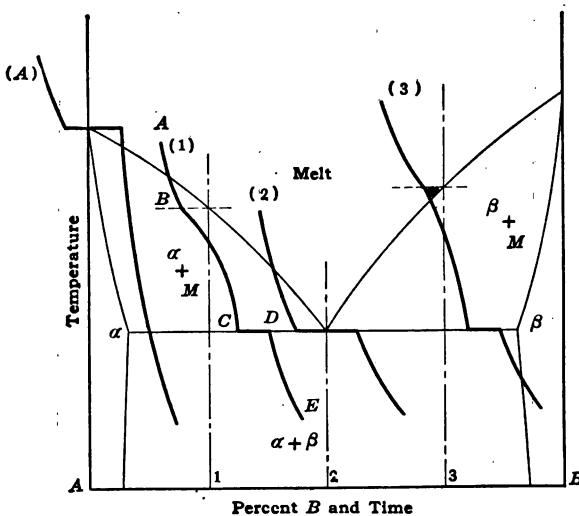

Fɪɢ. 78.—Cooling curves of an eutectiferous series.

of a pure metal because the eutectic, like the pure metal, solidifies at a constant temperature. This curve is shown at (2) in Fig. 78. The horizontal branch in this case corresponds to the simultaneous separation of *α* and *β*. A typical cooling curve of the intermediate alloys is given at (1). The branch *B–C* corresponds to the solidification of primary *α* while the branch *C–D* corresponds to the solidification of the eutectic. Points on the liquidus are determined, as before, by the first transitions, while the eutectic horizontal is determined by the temperature of the horizontals on the cooling curves. The end points of the eutectic horizontal could be determined, at least theoretically so, by noting the first compositions to show the horizontal

in the cooling curve although this determination does not give any great accuracy.[1]

Alloys of Type III. *Peritectic Series.*—The cooling curves of Type III alloys are shown in Fig. 79. Cooling curves of the pure metals and of the α solid solution are the same as those already described. The cooling curve of an alloy which passes through the peritectic reaction, such as alloy (2), indicates the successive steps in the solidification of the alloy. The first step is always the separation of the α solid solution, which gives the branch *B–C* of the cooling curve. At the point *C*, the peritectic reaction
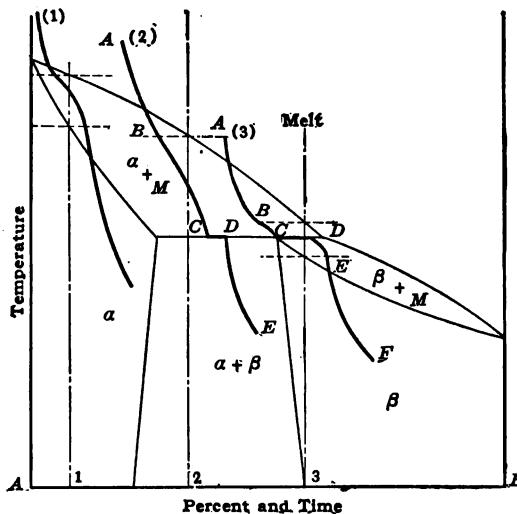

Fig. 79.—Cooling curves of a peritectic series.

between α and the melt commences, so that the temperature remains constant up to *D*. At *D* the peritectic reaction is completed and the alloy is entirely solid. Alloys, between the peritectic point and the transition point on the liquidus, solidify in three separate steps. The cooling curve of such an alloy is shown at (3). As before, the branch *B–C* corresponds to the solidification of the α solid solution, and the branch *C–D* to the peritectic reaction. The branch *D–E* corresponds to the further solidification of the alloy; *i.e.*, to the separation of the β solid solution.

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[1] For a more accurate method, see TAMMANN's "Method of Thermal Analysis."

Tammann's Method of Thermal Analysis.—This method was devised by Professor Tammann to assist in locating the end points of temperature horizontals, and such points as the eutectic point and the peritectic point.[1] To locate the eutectic point, a constant quantity of metal is used so that the "eutectic time," as given by the length of the eutectic horizontal of the cooling curve, will increase uniformly up to the eutectic point, where it becomes a maximum. The eutectic times are then plotted as
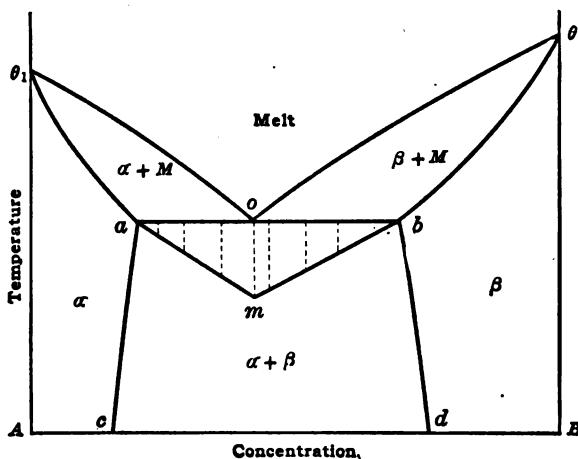

Fig. 80.—Tammann's method of thermal analysis.

verticals along the eutectic horizontal, and a line is drawn through the end points, as is shown in Fig. 80. The intersection of these two lines gives the eutectic concentration. Furthermore, the intersections of the two lines with the eutectic horizontal give the end points of the eutectic horizontal.[2]

In actual practice it is somewhat difficult to determine the exact duration of the solidification of the eutectic.[3] This is

[1] The method described is essentially for use with binary systems but has been extended to the investigation of ternary systems as well. See SAHMAN and VEGESACK, *Zeit.* Phys. Chem., 1907, Vol. 59, p. 257.

[2] For a more extended discussion, see TAMMANN, "Metallographie," 1914, p. 168.

[3] Tammann points out the necessity of correcting the "eutectic time" by an amount which will just eliminate the error due to thermal conduction along the pyrometer. This may be done by reconstructing the time-temperature as shown in the sketch. The true eutectic time is equal to *b–c'*. See TAMMANN, *Loc. cit.*
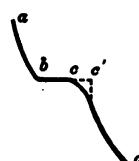
especially noticeable in the vicinity of the eutectic composition so that the true intersection point is not as well defined as could be desired and an error of some magnitude is introduced. The second source of error is the lack of homogeneity of the alloys containing large amounts of α and β, which causes the eutectic to enter at concentrations which actually are below the true saturation points of α and β.

Rosenhain has used the more accurate method of measuring the areas of the peaks of the inverse-rate and derived-differential curves which he obtained by using special precautions to insure uniform rates of cooling, but he states that "no very high degree of accuracy can be obtained, principally because the endpoint of an arrest is never sharply defined, and also because the conditions of heating and cooling cannot be kept absolutely constant from one alloy to another." If this method is used to determine the composition of the peritectic point, irregularities may be introduced due to the fact that the peritectic reaction has been stopped at an initial stage by reaction rims.

CHAPTER VI

PHYSICAL PROPERTIES

It is now well known that there is a definite relationship between the properties of metals and alloys and their constitution as determined by microscopical and thermal analysis. For example, it has been abundantly demonstrated that metals which form solid solutions are invariably harder, and have lower conductivities than would be computed for the composition from the law of averages. On the other hand, the properties of alloys which are mechanical mixtures are generally linear functions of the composition. These relationships are now so well established that the physical properties are commonly used in the study of alloys as a check on other methods of investigation.

Physical properties are also extensively studied to determine the possible scientific or industrial uses to which the metals or alloys may be put. In this way, new alloys are procured and methods of treatment are worked out which are best adapted to the production of the finished products. The following is intended to serve as a guide to metallographic work in both of these directions. In this discussion we shall consider specific volume and dilatation, electrical conductivity, magnetism, electrolytic potential, and thermo-electric force.

Specific Volume.—The density of a body is its mass per unit volume; the specific gravity is the weight of a known volume of the substance divided by the weight of an equal volume of water. Either of these quantities may be conveniently expressed as grams per cubic centimeter. The reciprocal of the specific gravity is called the specific volume which, inasmuch as it, and not the specific gravity, is a linear function of the composition,[1] is used in the study of the constitution of alloys. However, on account of the greater accuracy secured by determining the specific gravity, this measurement is the one which is usually made.

[1] OSTWALD, "Lehrbuch d. allgemeinen Chemie," Vol. 1, 3d Ed., p. 782.

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Specific gravities of metallic alloys are commonly determined by the Archimedean method; *i.e.*, by comparing the weight of the body to the weight of water which it displaces when completely immersed. This is done by weighing the body in air and then in water, whereupon the specific gravity is given by

$$S = \frac{W}{W - W'} (G - \lambda) + \lambda$$

where S is the specific gravity (referred to water at 4°C.), W and W' are the weights of the specimen in air and in water respectively, G is the density of the water at room temperature and λ is the density of the air. The specimen, after having been carefully cleaned in absolute alcohol and dried, is suspended from the balance by a fine platinum wire[1] and weighed with an accuracy of at least 0.1 milligram. The depth of immersion of the platinum wire must be kept constant while the readings are being taken.

The specific volume of pure metals bears a direct relationship to the atomic weight, as the atomic volume (atomic weight/ specific gravity) is a periodic function of the atomic weight. The specific volume is not strictly constant as it is affected by casting, drawing and annealing, as has been shown by Kahlbaum and Sturm.[2] They found that a platinum cylinder, as cast, had a specific gravity of 21.2137, while the same, when rolled into a bar, had a specific gravity of 21.4314. The increase on rolling is due to the closing up of the cavities which are always present in a casting. Further drawing of the bar to a wire, cold, reduced the specific gravity to 21.4136, which is supposed to be due to the derangement of the "closest packing" of the atoms by the formation of slip bands in the crystals.[3] On annealing, the specific gravity was restored to 21.4314, by replacing the closest packing.

It has also been assumed that this derangement of the closest packing converts the metal along the slip bands into the amorphous state (Beilby's "amorphous phase" theory), a contention which has received considerable support from the work on bismuth, a metal whose specific gravity is greater for the liquid state than

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[1] The diameter to give the most uniform results is 0.32 mm. according to Kahlbaum and Sturm, *Zeit.* anorg. Chem., 1905, Vol. 46, p. 217.

[2] *Loc. cit.*

[3] This subject will be considered under "Plastic Deformation."

for the solid. Spring[1] and, again, Johnston and Adams[2] have shown that mechanical deformation increases, and subsequent annealing decreases, the density of bismuth. This is just what would be expected in the light of the amorphous phase theory from the known volume change of bismuth on melting.

Metals, like other substances, expand on heating. The law is expressed as follows:

$$V_t = V_0(1 + \alpha t + \beta t^2) \text{ or simpler, } V_t = V_0(1 + \alpha t),$$

where V_0 is the volume at 0°C., t is the temperature, and α and β are constants. If no polymorphic transformation point is passed through the expansion is continuous to the melting point.

On melting, the majority of metals undergo a sudden expansion, as given by the following table taken from the work of Toepler.[3] The volume changes are given in cubic centimeters per gram on melting.

TABLE 9.—VOLUME CHANGES OF PURE METALS ON MELTING

	Ccm. per gm.
Sodium	0.027
Potassium	0.030
Zinc	0.010
Cadmium	0.0064
Mercury	0.0026
Aluminum	0.019
Silicon	Less than 0
Tin	0.0039
Lead	0.0034
Antimony	0.0022
Bismuth	−0.0035
Selenium	0.018
Tellurium	0.012

Bismuth and silicon are the principal exceptions to the general rule.

Of the metals which have been investigated, it has been found that tin, lead, zinc, antimony, aluminum and copper continue to expand above their melting points much the same as they do in the solid state.[4]

[1] *Journ. Phys. Chem.*, 1903, Vol. 1, p. 593.
[2] *Zeit.* anorg. Chem., 1912, Vol. 76, p. 274.
[3] *Wied. ann.*, 1894, Vol. 53, p. 343.
[4] PASCAL, *Comptes Rendus*, 1914, Vol. 158, p. 414; *Rev. de Met.*, 1914, Vol. 11, p. 469. A peculiar irregularity in the expansion of molten tin at 620°C. was noted—a difficult effect to explain.

Specific Volume and Binary Alloys.—Measurements of the specific volume have not proven very satisfactory for the determination of the constitution of binary alloys, principally because volume changes due to alloying one metal with another correspond too closely to the theoretical change, irrespective of the behavior of the two metals towards each other. Greater success has been attained by following the change of volume with temperature (dilatation) and there seem to be possibilities for future success in this direction.

Failure in the past has been to some extent due to lack of understanding of the laws governing the specific volumes of alloys and fortunately we have, in the work of Guertler,[1] a statement of the possible relations between the specific volume and constitution of binary alloys. With the aid of this work many of the data which have been obtained, especially by dilatometric methods, and which are otherwise not very readily interpreted in terms of changes in constitution, can be utilized in the study of the behavior of binary alloys.

The specific volume of a heterogeneous mixture of two phases, on the assumption that there are no pores or hollow spaces, is a linear function of the concentration. The graphical representation of this function would be a straight line running from the specific volume of one phase to that of the other. Aside from this, as Guertler points out, the grain size of the aggregate also has an influence on the specific volume of the mixture. Thus in a heterogeneous mixture, such as a fine grained eutectic, the specific volume is slightly greater than that calculated for its composition. This variance becomes more noticeable as the grain size of the aggregate decreases. Accordingly, the variation would be more pronounced in the case of sorbite than in pearlite, and in turn, more so for troostite than for sorbite, microconstitutents of the iron-carbon alloys. These variations are in reality very small and need be considered only in the case of very accurate measurements. As the ordinary determination is subject to an error of 1 per cent. it is obvious that this point need be seldom considered. The curve for a series of homogeneous solid solutions is likewise linear with the composition so that, with this method, one cannot distinguish between heterogeneous and homogeneous alloys.

The presence of intermetallic compounds is shown on the

[1] "The Specific Volume and Constitution of Alloys," *Journ.* Inst. Met., 1913, No. 2, p. 175.

curve as the intersection of two straight lines running from the compound to the two adjacent phases. It has been shown by Maey [1] that compounds can have either greater or lesser specific volumes than would be calculated from their compositions. The early work by this method was not very successful in locating intermetallic compounds, however, as it has been shown by subsequent work that only rarely did the compound thus located, actually exist; and at times the substance supposed to be the "compound" was shown to consist of several different phases.

More recently Frilley[2] has determined the densities of the alloys of silicon with manganese, chromium, nickel, iron, tungsten, copper, and aluminum, but again there is a lack of agreement between his results and the constitution as determined by microscopical and thermal analysis.

The Effect of Temperature: *Dilatation.*—The dilatation of binary alloys is considered somewhat in detail by Guertler who discusses typical specific volume–concentration–temperature surfaces for several different types of alloys. This method is not regarded as one of the standard methods for locating melting points, however promising it may become when suitable experimental means are available, but it has, at least, been used in the study of transformations in the solid state. Some of the cases in which this method has been employed will be considered later. Desch has suggested determining the linear coefficient of expansion as offering a promising means of studying the constitution.

Electrical Conductivity.—Conductivity determinations have met with far greater success because, for some reason not as yet understood, metallic conduction of solid solutions and of simple mechanical mixtures is fundamentally different. Likewise, in metallic conduction, intermetallic compounds differ radically, as a rule, from either a solid solution or a mechanical mixture and are more nearly similar to the pure metals. For these reasons conductivity measurements bring out, as we shall see, the true character of an alloy and give a very valuable control of the thermal and microscopical determinations.

The passage of an electric current through metallic conductors is a matter of common knowledge; but the manner in which the

[1] MAEY, *Zeit.* f. physik. Chem., 1899, Vol. 29, p. 119; 1901, Vol. 38, p. 292.

[2] *Rev. de Met.*, 1911, Vol. 8, p. 457.

current is conducted, in contrast to the same phenomenon in electrolytes and gases, is not as yet clearly understood. According to the electron theory of Drude,[1,2] the current is assumed to be conveyed by electrons moving between the molecules, so that the conductivity of a metal would depend upon the number of electrons in unit volume and also upon the speed with which they move under unit force. In the light of later research, Thomson has pointed out that this theory is not tenable. His contention is supported largely by the experiments of Onnes on the "super conductivity" of metals at the temperature of liquid helium, as it is hardly conceivable that the number of electrons and their velocity would increase in such a remarkable manner with drop in temperature. The number of electrons which would be required for the transport of the current in such metals as copper and silver is also not compatible with other physical properties of these metals.

A somewhat different theory is the one recently advanced by Thomson[3] who supposes that bodies are built up of dipoles, which are analogous to molecular magnets. Each dipole consists of a positive and a negative charge separated by a small distance, the negative charge being an electron. The function of the electric force is to cause the dipoles to point all in the same direction and form "chains," while the conduction of electricity results from the action of the doublets on the atoms by pulling electrons out of one atom and into the next. The current continues to flow as long as the thermal agitation is insufficient to break up the chains. The difference between conductors and non-conductors is that the electrons of the latter are better able to resist the pull. According to this theory, the quantity of electricity passing per second would be $N.e.p.$ where N is the number of chains passing through unit area, p is the number of electrons passing along each chain and e the charge carried.[4]

When considering the conductivity of metals and alloys it is

[1] P. DRUDE, *Ann. Physik.*, 1900, Vol. 1, p. 566; Vol. 3, p. 369; 1902, Vol. 7, p. 687.

[2] To disprove an older theory which assumed that electricity was carried by matter, a current was passed through composite conductors of copper, silver, etc., which were later analyzed. No migration of matter could be shown. See GENO KINSKY, *Zeit.* Elektrochem., 1908, Vol. 12, p. 406.

[3] May Lecture, *Journ.* Inst. Met., 1915, No. 2, p. 3.

[4] A general discussion of electrical conductivity is given by STEINMETZ, *Trans.* Am. Electrochem. Soc., 1908, Vol. 11, p. 81.

customary to use both the specific resistance and the specific conductivity. The specific resistance is the resistance in ohms of a column one centimeter high with a cross sectional area of one square centimeter. The specific conductivity, called "conductivity" for short, is the reciprocal of the specific resistance. In general, the resistance of a conductor is given by $R = \delta\dfrac{l}{q}$ where l is the length, q is the cross sectional area, and δ is the specific resistance. Now, according to Ohms Law, $R = \dfrac{E}{I}$; hence the specific conductivity equals $\dfrac{lI}{Eq}$.

It is customary to measure resistance in ohms where 1 ohm = 1 volt/ 1 ampere. According to Ohms Law then, the resistance of a conductor is the number of volts required to cause the flow of 1 ampere, while the conductivity is the number of amperes of current that will flow under a pressure of 1 volt.

Conductivity is also referred to the conductivity of mercury at 0°C. which is taken as unity. In order to convert into conductivity expressed as the reciprocal of the specific resistance, it is necessary to multiply by the factor 10,630.

There are two general methods in use for measuring conductivity, both of which depend upon the measurement of resistance.

1. The measurement is made, following the definition, by measuring the actual dimensions of the test bar and the resistance, or

2. By comparing the resistance of the test bar to that of a standard bar of the same dimensions, whose resistance is known.

The former method is the one which is most commonly employed. The form of the conductor should be simple, preferably a wire. In many cases the alloy is too brittle or too weak to be drawn into the form of a wire, and it becomes necessary to cast a round test bar for the purpose. A smooth and uniform rod can be obtained for this purpose, according to Stepanoff,[1] by drawing the molten metal up into a previously heated tube of glass or porcelain which has been coated on the inside with lampblack. This method gives a bar which is dense and homogeneous—the two chief conditions which must be satisfied. The cross sectional area is obtained from the length of the wire and its

[1] *Zeit.* anorg. Chemie., 1912, Vol. 78, p. 1.

volume, as determined according to the methods customary in physics.

The set-up of the apparatus should be such that the resistance of the leads and their contacts with the test bar may have the smallest influence possible on the measurements.[1] In the case of good conductors in the form of bars or rods, both of these effects are eliminated by means of a shunt circuit, the leads of which are soldered to the bar or inserted in small drill holes.

In making determinations of the conductivity, it is necessary to consider various external influences, of which the most important is the temperature. The conductivity of most of the pure metals decreases about 0.4 per cent. for an increase of 1°C., so that if the conductivity is expressed to within 1 per cent. the temperature should be given to less than 1°C. A magnetic field can be said to have no appreciable effect on the conductivity, although in the case of the strongly magnetic metals it does have a small influence. Strange to say, the conductivity of bismuth is changed by the introduction of a magnetic field, the effect of which is more pronounced at the lower temperatures. This effect is even used as the basis of a method for determining the strength of a magnetic field. Mechanical stresses and pressure have little influence on the conductivity, but impurities which are very commonly present even in so-called pure metals, generally lower the conductivity. If the impurities are in solid solution in the metal, the depression of the conductivity is all out of proportion to the amount of impurity present; for example, the addition of 1 per cent. of copper (by weight) lowers the conductivity of gold from 48 to 32.5 or by 31 per cent. This fact is too frequently overlooked by physicists with the result that considerable accurate but untrustworthy determinations have been made on insufficiently defined materials.

Mechanical work has an influence on the conductivity,

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[1] For details of the measurements as well as necessary precautions, physics manuals should be consulted. The "Handbuch der Arbeitsmethoden in der anorganischen Chemie" contains all the important methods, not only for the determination of conductivity but of other physical constants such as magnetism, electrolytic potential, density, etc. In accurate determinations the resistance is measured by the Wheatstone bridge, the Thompson double bridge, which is somewhat less sensitive but which eliminates contact and lead resistances, and the potentiometer, which is capable of measuring resistances (0.01 ohms to 0.001 ohms) to the fifth decimal place (WHITFORD, *Physics Rev.*, 1912, Vol. 15, p. 145).

chiefly through the change in structure which is produced. Wires can have either a greater or lesser (generally lesser) conductivity than cast metals, the difference being as great as 1 per cent. If the casting shows a lower conductivity, the general assumption is that it is not homogeneous.[1] Heat treatment, which likewise changes the internal structure, has an influence on the conductivity.

Conductivity of Binary Alloys.—The relationships between conductivity and constitution of binary alloys, which we shall consider here, are largely those which have been laid down by Le Chatelier,[2] and Guertler,[3] based largely on the experiments of Matthiessen.[4] This study has since been continued by Kurnakow and Zemczuzny,[5] and others, who have determined the conductivities of a number of binary series whose constitution had already been determined by thermal and microscopical analysis.

We shall first consider alloys of Type IIa, whose components are insoluble in each other. The questions which first arise are as to the method of expressing the composition of the alloy and the unit to use to express the electrical conductivity, whether specific resistance or specific conductivity. While opinion on these questions seems to vary considerably, it is perhaps safe to say that the specific resistance of alloys of metals which are insoluble in each other is a linear function of the composition by volume. It is true that conductivity is also used in this connection, but, as Benedicks has pointed out, a theory can be established only on the basis of specific resistance. As we have seen, resistance depends on the volume, so if the two metals, forming the mixture, were to run in parallel continuous rods, the resistance would be the mean of the two resistances; but in reality, the metals form crystallites which are distinct but intergrown so that the resistance measured will depend on the accidental

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[1] We shall see later that evidence has been advanced to show that at least one metal, iron, seems to be but little affected by mechanical work, even though it be quite severe.

[2] *Revue* Generale des Sciences, 1895, p. 529.

[3] *Zeit.* anorg. Chemie., 1906, Vol. 51, p. 397; 1907, Vol. 54, p. 58. Jahrbuch f. Radioaktivität und Elektronik, 1908, Vol. 5, p. 17. *Journ.* Inst. Met., 1911, No. 2, p. 135.

[4] Phil. *Trans.* 1858, Vol. 148, p. 343; 1860, Vol. 150, p. 85; 1864, Vol. 154, p. 167.

[5] *Zeit.* anorg. Chemie, 1908, Vol. 60, p. 1.

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arrangement of the particles.[1] So far it has been impossible to give definite answers to the above questions. Several curves of this kind are shown in Fig. 81.

The ultimate arrangement of the particles plays an important role in determining the conductivity; thus it has been found that rods composed of tungsten powder and thorium oxide powder show metallic conduction when the insulator granules are coated with an envelope of tungsten, but not so when the tungsten
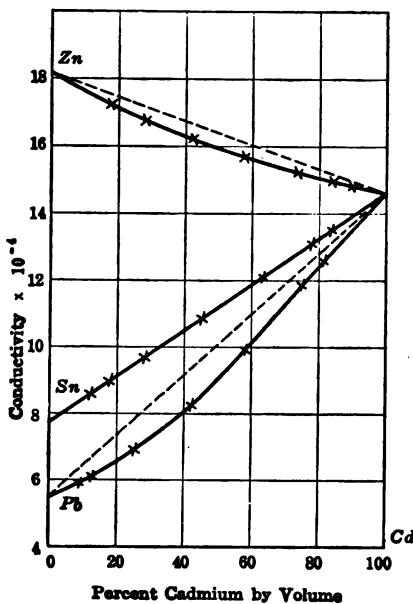

FIG. 81.—Conductivities of cadmium alloys.   (*Guertler.*)

particles are covered with a thin film of thorium oxide.[2] In the same way copper sulphide, as a film or "cement" about copper grains, can increase the resistance of copper out of proportion to the amount of sulphur present.

[1] Lichtenecker has calculated the resistances of alloys of this type and his results agree closely with those found by experiment, but as Guertler points out, his solution holds good only in case the difference in conductivity of the two metals is small. In such a case the unit used (resistance or conductivity) would be immaterial and it would be difficult to determine the exact function in either case. See LICHTENECKER, *Phys. Zeit.*, 1910, Vol. 10, p. 1005.

[2] FINK, *Met. & Chem. Eng.*, 1916, Vol. 15, p. 464.

We next come to alloys of Type I. In this case, it will be remembered, the two metals form a continuous series of solid solutions. Here again it is necessary to consider the units to represent conductivity and composition and again the same difficulties are encountered. The case is somewhat simpler than the preceding one, as the relationship between the electrical conductivity and composition is very well known and it is relatively immaterial which units are used to express it. However, conductivity is generally used on account of its more vivid representation of the function. It is at least obvious that the same
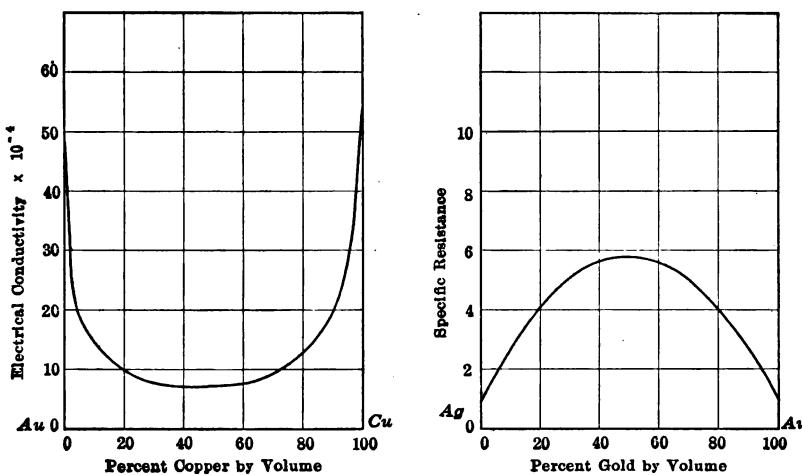

Fig. 82.—Conductivities of the gold-copper alloys. Resistances of the silver-gold alloys. (*Guertler.*)

need for representing composition by volume per cent. does not exist here, as it does in the previous case, so that either weight per cent. or atomic per cent. may be used, according to preference.

The variation in conductivity, as a function of the composition, is represented by a deep U-shaped curve running between the conductivities of the two pure metals. An example of this case is furnished by the gold-copper alloys, the conductivities of which are shown in Fig. 82. The addition of even a small amount of copper to gold, in spite of the higher conductivity of the copper, causes a remarkable decrease in the conductivity, altogether out of proportion to the amount of copper added. Alloys containing about equal parts of gold and copper have conductivities of

about one-sixth that of pure gold.[1] The curve, showing the variation of the specific resistance with composition, passes through a maximum corresponding to the minimum of the curve for the specific conductivity. A curve of this type is also shown in Fig. 82.[2]

If the two metals are partially soluble in the solid state, such as in Types II *b* and III *a*, we have three groups of alloys to consider; *e.g.*, the two series of solid solutions and the heterogeneous mixtures of the saturated solid solutions. The conductivity over the ranges of solid solutions varies in a manner which is charac-
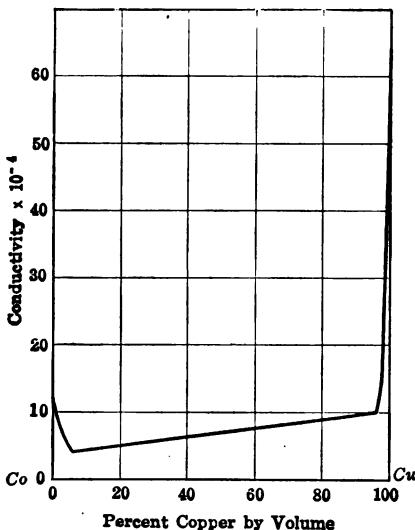
FIG. 83.—Conductivities of the cobalt-copper alloys. (*Guertler.*)

teristic for this kind of alloys and drops sharply from the conductivity of the pure metal to that of the saturated solution. The conductivity of the intermediate alloys varies in a manner similar to that discussed for alloys of Type II *a* and therefore the curve is practically linear between the two points, unless there is considerable difference between the conductivities of the two

[1] As Rosenhain says, apropos of the electron theory of metallic conduction, "it is not easy to see why the simultaneous presence of two or more kinds of atoms or molecules—all of whose attendant electrons are supposed to be alike—should produce such striking effects."

[2] There is a striking similarity between this curve and the one showing the variation in hardness, which is characteristic of the close relationship between these two properties.

solutions. Fig. 83 gives a typical example taken from the work of Guertler. Here again it would be advisable to compute composition by volume per cent.

If the (partial) solubility of the two metals is limited to one side of the diagram, an L-shaped curve is usually obtained, the vertical branch corresponding to the limited series of solid solutions and the horizontal branch to the mixtures of the saturated solid solution and the other pure metal.

Intermetallic compounds are characterized on conductivity-concentration curves by sharp cusps upwards, whose maxima fall at the compositions of the compounds. Guertler suggests, in this case, that the diagram should be subdivided into parts bounded by the pure metals and the one or more compounds, and that each part be considered separately. An interesting and highly important point, in this connection, is that, so strong is this tendency of compounds to conduct like pure metals, intermetallic compounds give rise to maxima on conductivity-concentration curves, even though the compound is in an isomorphous series of solid solutions. We shall see later that intermetallic compounds may be detected in this way even in molten alloys, as long as the compound is at least partially associated.

From what has just been said it is evident that conductivity-concentration curves can be used to study the constitution of binary alloys, although the results obtained by this method are in the main subordinate to those of the thermal and microscopical analyses. The most striking feature of these curves is the rapid drop near the pure metals (or intermetallic compounds) which occurs if the added metal forms solid solutions. This offers a very delicate means of ascertaining whether or not small amounts of additions go into solution, and, to a lesser extent, the limits of saturation. As applied to the former this method may be said to be the most delicate as yet used.

The Effect of Temperature.—The conductivity of metals and alloys follows the well-known law of metallic conduction and decreases with rise in temperature. In terms of resistance, the effect of temperature can be stated as follows:

$$R_t = R_o (1 + \alpha t + \beta t^2)$$

where R_t and R_o are the resistances at $t°$ and $o°$ respectively and α and β are constants. Over small intervals it is sufficient to

consider $\beta = 0$. The resistance increases according to the above law up to the melting point, at which temperature it changes abruptly according to the general rule that the denser state is the better conductor. Conversely, it is known that the resistance decreases with drop in temperature, at least down to 4°C. absolute which is the lowest temperature at which measurements have been made. At this temperature the resistance attains remarkably low values, which gives the "super conductivity" of Onnes.[1] The passage of a metal or alloy through an allotropic transformation produces a corresponding change in the resistance by means of which effect, certain transformations have been studied.

The effect of temperature on the resistance of an alloy whose components are in solid solution is of the same general nature except that it is modified in two important respects. First of all, temperature has a much smaller effect on the resistance and, secondly, the resistance decreases with drop in temperature only to a certain point. Further decrease in temperature is without effect on the resistance. This has led to the discovery that the resistance of solid solutions is composed of two parts (1) a resistance which depends on the nature of the metals in solution and (2) a "solution resistance" due to solid miscibility and which is independent of the temperature. It is only the former resistance that varies in value with temperature, and with drop in temperature, as soon as the resistance drops to the solution resistance a further decrease of temperature is without effect on the resistance.[2]

These relationships make it perfectly possible to determine the complete constitution diagram by means of temperature-conductivity measurements. This would be done by measuring the conductivities of a sufficient number of alloys at successively increasing temperatures, up to and including the liquid state. The conductivity-temperature-concentration surface would show, by certain typical features such as were discussed under thermal analysis (and again under specific volume), the transformation ranges, ranges of solidification, etc., according to which the complete diagram could be drawn.

[1] For an account of this work, see SCHUELER, *Zeit.* Elektrotech., 1914, Vol. 35, p. 1011.

[2] See CLAY, *Jahrbuch* d. Radioaktivität und Elektronik, 1911, Vol. 8, p. 383.

One of the chief advantages of using electrical conductivity measurements as a means of studying the constitution, is the possibility of holding the alloys at any temperature for a sufficient length of time to insure equilibrium before making the measurement. A second advantage is that transformations in the solid state can be brought out in a very pronounced manner, due chiefly to the great sensitivity of the present methods of measuring resistance.[1] An example of a case which illustrates the value of the method, is to be found in the bismuth-thallium alloys. Whereas the thermal effect accompanying the transformation of thallium at 225° is very weak,[2] the temperature-resistance curve shows an abrupt discontinuity. Furthermore, this method makes it possible to follow the effect of the addition of small amounts of bismuth on the transformation point of thallium.

The molecular character of molten alloys has been investigated by determining the conductivity-concentration curves at temperatures above the liquidus. This work has been done largely by Bornemann and his co-workers[3] and has verified to a remarkable extent, the conclusions drawn from the conductivity-concentration curves of alloys in the solid state.

Summarizing, it can be said that these curves bring out the following points:

1. Complete miscibility is usually shown by a simple U-curve from one pure metal to the other. This is not always the case for completely soluble metals, as the conductivity of the lead-tin alloys in the molten state is proportional to the composition, as it is for the solid state.

2. An undissociated compound is brought out on the conductivity and temperature coefficient curves by either maxima or minima (usually minima). If the temperature is raised above the melting point, and conductivity-concentration curves plotted for successively higher temperatures, it is noted many times that the cusp gradually diminishes and finally disappears at a temperature which is assumed to be the dis-

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[1] GUERTLER, *Zeit.* Elektrochem., 1912, Vol. 18, p. 601.

[2] LEVINE, *Zeits.* anorg. Chemie, 1905, Vol. 45, p. 31.

[3] See BORNEMANN and MÜLLER, *Met.*, 1910, Vol. 7, pp. 396, 655, 730.
Intern. Congress Düsseldorf, 1910, Division Theoret. Met., p. 14.
BORNEMANN and RAUSCHENPLAT, *Met.* 1912, Vol. 9, p. 473.
BORNEMANN and WAGENMANN, *Ferrum*, 1913, Vol. 11, p. 276.

sociation temperature of the compound. This method offers the only means known at present of locating compounds which occur in the liquid state, although there is a possibility that viscosity measurements will give the same or similar indications.

3. Gaps in liquid miscibility can be located by this means as the appearance or disappearance of one of the phases produces a marked change in the conductivity.

4. Likewise, points on the solidus and liquidus can be accurately determined.

5. These measurements have also brought out a difference in the conduction of dilute and concentrated metallic solutions.

Among other things it was noted that the metallic compounds, when molten, usually have negative temperature coefficients of electrical resistance.

Northrup has investigated the electrical conductivity of a number of metals at high temperatures, including mercury, cadmium, lead, zinc, tin, bismuth, antimony, copper, aluminum and gold.[1] He found a decrease in the conductivity of all the metals named, on melting, with the exceptions of antimony and bismuth. Above the melting point, the resistance was found to increase as a linear function of the temperature, with the exception of zinc, cadmium and antimony. The ratio of the coefficient of resistance to that of cubical expansion was found to be approximately constant, for the molten state.[2]

The Temperature Coefficient.—The temperature coefficient, usually taken as the percentage decrease in conductivity or increase in resistance between 0° and 100°C., gives the same information regarding the constitution of metallic alloys as the conductivity, and, in certain instances, in a much clearer manner. The measurement of the temperature coefficient possesses one distinct advantage in that it is independent of the dimensions of the test piece and of pores or blowholes. On this account even irregularly shaped reguli can be used in the determination of the temperature coefficient-composition curve.

Two different equations are used to express the temperature

[1] *Met. & Chem. Eng.*, 1914, Vol. 12, p. 340.

[2] See also WAGNER, *Ann. Physik.*, 1911, Vol. 33, p. 1484, who found the ratio of the conductivity of solid Hg to molten Hg at the melting point, to be 4, while the same ratio for Pb, Zn, Sn, Cd, Tl, Te was 2, and for the alkali metals 1.5, and for Bi and Ga, 0.5 (Bi and Ga expand on solidifying).

coefficient, one for conductivity and the other for resistance, as follows:

$$C = \frac{\lambda0 - \lambda100}{\lambda0} \times 100$$

where C is the temperature coefficient of conductivity, $\lambda0$ and $\lambda100$ are the conductivities of the test bar at 0° and 100° respectively, and

$$R_t = R_o(1 + \alpha t)$$

where R_t and R_o are the resistances at temperatures $t°$ and 0°, and α is the temperature coefficient of resistance.[1] C has a value of 27 to 31 for pure metals and remains fairly constant for alloys which are heterogeneous mixtures of the two pure metals. C drops very sharply if the two metals form solutions and gives the characteristic U-shaped curve. As the value of C is quite high for intermetallic compounds, nearly as high as for pure metals, the presence of an intermetallic compound is brought out very clearly as a maximum on the temperature coefficient-concentration curve. This feature is so pronounced that the temperature coefficient-concentration curve serves as a valuable check on the conductivity concentration curve. An example of the special utility of temperature coefficient measurements in showing compounds which are missed by conductivity measurements is furnished by the magnesium-silver alloys. The compound Mg_3Ag would not be noticed on the conductivity curve but, on the temperature coefficient curve, it is brought out as a sharp maximum at 25 atomic per cent. silver.

Practical Considerations.—There are three classes of conductors which are of commercial importance, viz., conductors, resistances, and insulators.

It is well known that the best conductors of electricity are, in the order of their conductivities, silver, copper, gold, aluminum, zinc and iron. Of these, silver and gold can be eliminated for ordinary uses on account of their high cost. Copper is much less expensive and combines high conductivity with mechanical strength very satisfactorily and is the material most commonly used today. Aluminum conducts 62 per cent. as well as copper and possesses the advantage over copper of extreme

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[1] Von Pirani suggests the form $\frac{dR}{dT} / R$.

Ber. physik. Ges., 1911, Vol. 9, p. 929.

lightness, so that for equal weights, aluminum conducts about 2.6 times as much electricity as copper. It is found in practice that, to carry the same current, an aluminum conductor should be about 25 per cent. larger in cross section than a copper conductor

Iron is now used as third rails because it is a fairly good conductor, can be had in large cross section, and resists the wear of the shoe. Obviously purity of the iron is a decided advantage in this case, although a small amount of carbon is needed to give resistance to abrasion. Iron wire is also used in telephone and telegraph service where only small currents are to be carried.

Zinc is not used to any extent as a conductor except perhaps as a war substitute. Its conductivity and low melting point suggest its use in fuses for electrical circuits.

As for obtaining alloys with higher conductivities than the metals now in use, from the following considerations it is evident that such a thing is impossible. On the basis of the known constitution diagrams, Guertler[1] points out that the metals with relatively high conductivities form solid solutions and that intermetallic compounds which might possibly have miraculously high conductivities are entirely lacking. Furthermore, the great majority of intermetallic compounds have very poor mechanical properties, which fact alone would be sufficient to exclude them from commercial use.

Materials used for resistances vary considerably with the requirements. Rheostats used in street railway service are generally made of cast iron grids and are designed to carry a heavy current. Band iron is also used for heavy work. Resistances for scientific instruments have entirely different requirements, which are met in a very interesting fashion.

A comparison of the conductivity-concentration curve and the temperature coefficient-concentration curve shows that both curves have the same shape. Those alloys which have the greatest resistance also vary the least with temperature. It is a happy coincidence that those alloys which, on account of their greater resistance, would be selected for resistance wire, also have a very low temperature coefficient. On this account alloys, such as constantan, manganin, etc., are of peculiar im-

[1] Met., 1908, Vol. 5, p. 292.

portance in the construction of constant resistances for scientific and technical purposes.[1]

Resistance wire is used at present in considerable quantities for heating purposes. The desirable properties here are fairly high resistance and ability to operate continuously (1000 hours) at temperatures up to 1000°C. The most important alloys of this class are the nickel-chromium alloys, commonly known as "nichrome."

Insulators are not found among the metals so will not be considered here.

Magnetic Properties.—Metals and alloys when placed in a magnetic field either concentrate the lines of force so that a greater number pass through a given volume, or else they disperse the lines of force, with the opposite effect. Metals and alloys of the first class are paramagnetic and of the second class, are diamagnetic. The metals of the iron group, the so-called ferro-magnetic metals, iron, nickel, and cobalt, constitute a special group of the paramagnetic metals and are characterized by being exceptionally magnetic. They are by far the most important group of metals which have been studied in this connection, and the loss of magnetism of these metals and their alloys at higher temperatures have been of particular interest to the metallographist as a demonstration of their allotropy. Of more recent date the magnetic properties of the weakly magnetic metals have been studied and their constitutional relationships determined.

The property which is generally employed in metallographic work to compare the magnetic behavior of metals and alloys is the susceptibility, which is sometimes expressed as the specific susceptibility, K, or the susceptibility divided by the specific gravity. This latter value gives the relative effect of each molecular magnet, so to say, in concentrating or dispersing the lines of force. The susceptibility is the ratio of the induced magnetism, I, to the magnetizing force or original field strength, H. I, for strongly magnetic substances, is generally determined by means

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[1] The temperature coefficients of resistance of a number of metals and alloys have been determined by Somerville, including Ni, W, Mo, Au, Ag, Cu, Fe, Al, Mg, C, nichrome, manganin, constantan, "advance," "excello," "superior," and "ia ia," over a range from 0° to 1000°C The originals should be consulted for data. The variation in the resistance of constantan was found to be under 1 per cent. up to 600°C. *Phys. Rev.*, 1910, Vol. 30, p. 532 and Vol. 31, p. 261.

of a magnetometer, such as the one described by Gray and Ross for their work on magnetism.[1] A magnetizing solenoid is placed with its long axis perpendicular to the magnetic meridian and at a distance, d, from its middle point to the magnetometer, which is on the longitudinal axis extended. The magnetometer used is a small horseshoe magnet, suspended by a fine fibre with a mirror attached, by which the deflection may be measured. Deflections of the mirror are determined by a lamp and scale in the usual manner. The field of the solenoid, whose magnetic effect must be eliminated, is balanced by means of compensating coils until there is no deflection of the magnetometer. The field strength within the solenoid is given by the formula

$$H = \frac{4\pi N}{10} \frac{i}{L}$$

where N is the number of turns to the length L and i is the magnetizing current in amperes. To measure the induced magnetism of the material, the test bar is placed within the solenoid along the central axis, with its middle point also at a distance, d, from the magnetometer. From the deflection of the mirror, I may be calculated from the formula

$$I = \frac{S\ d^3}{4\ a\ B} H_h,$$

where S is the scale reading, a is the distance from the scale to the magnet, B is the volume of the test bar and H_h is the value of the earth's field in gausses. The distance d must be appreciably greater than the length of the test bar. The susceptibility is then equal to $\frac{I}{H}$. The solenoid may be made large enough to contain an electric furnace for making determinations at elevated temperatures, in which case it is wound on a water jacket to prevent over heating the coils. The additional advantages of the magnetometric method are its rigidity, accuracy and simplicity.

In technical practice it is the total number of lines of force, instead of the induced lines of force, traversing unit cross section of the material which is determined. In this case B, the total number of lines, is equal to $H + 4\pi I$ The ratio of B to H is known as the permeability μ, which may also be calculated from the susceptibility from the formula $\mu = 1 + 4\pi\kappa$.

These measurements may be extended to the study of the mag-

[1] *Proc.* Royal Soc. of Edinburgh, 1910, Vol. 29, p. 182.

netism of weakly magnetic substances by substituting the induction balance for the magnetometer to measure the magnetic effect.[1] The apparatus also permits the use of an electric furnace for the investigation of the effect of temperature on the susceptibility. A null method for determining the susceptibility of weakly magnetic metals and alloys has been described by Mendenhall and Lent.[2] This apparatus was used in their studies of the magnetic properties of bismuth, tellurium, thorium and their alloys.

The Magnetic Properties of Metals.—The power of the metals of the iron group to concentrate magnetic lines of force varies considerably with the strength of the field in which they are placed. In very weak fields this is not as pronouced, but as the field strength further increases, the magnetization increases, more rapidly at first than the field strength, and then more gradually until the "saturation point" is reached. Above this point the material cannot be further magnetized, however strong the field may be, so the susceptibility gradually decreases with the increase in H. There will be occasion later on to refer to the magnetic properties of these metals, and principally iron, so they will not be further considered at this place.

The magnetic properties of a large number of the weakly magnetic metals have been systematically studied by Honda, chiefly for the purpose of examining the periodicity of the magnetic properties of the elements and the variation of the susceptibility with temperature and field strength. It was found that the susceptibility of over half of the elements examined was independent of the field strength, but the author concluded that without doubt the variation in the susceptibility of the others was merely apparent and that for chemically pure elements (free from iron) the susceptibility would be independent of the field strength.[3] Acording to this, if an element were to show a variation in susceptibility with change in the field strength, the presence of iron would at once be indicated. In order to get a direct comparison of the magnetism of the elements the specific sus-

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[1] HONDA, *Ann. Physik*, 1910, Vol. 32, p. 1027.

[2] *Phys. Rev.*, 1911, Vol. 32, p. 406. For the method of Meslin, see *Comptes Rendus*, 1905, Vol. 140, p. 1683.

[3] This has been verified by OVERBECK (*Ann. Physik*, 1915, Vol. 46, p. 677) who found that alloys of Cu-Zn which showed variations in the susceptibility with field strength and "metamagnetism," also contained traces of iron.

ceptibility was used. By arranging the elements in the periodic system according to Mendeleieff and plotting the specific susceptibility against the atomic weight, a decided periodicity was brought out.

The Effect of Temperature.—A characteristic common to all ferromagnetic substances is that the magnetism disappears if the substance is heated. The temperature at which this ccurs is typical for each substance and is given in Fig. 84 for the metals iron, cobalt and nickel, in which the specific magnetism, I, is here plotted against temperature. These curves show that I is practically independent of the temperature. The magnetic transformation of pure iron is accompanied by a small heat effect so
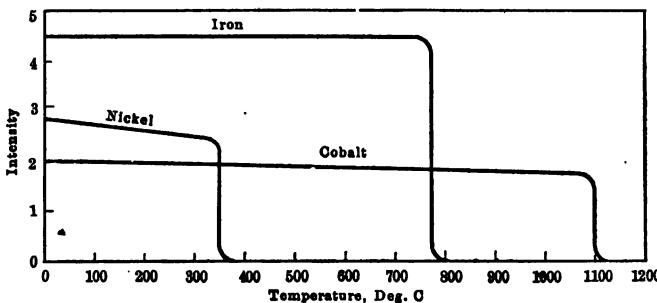
Fig. 84.—Magnetic transformation of iron, nickel and cobalt.

that it can be traced with the aid of thermal analysis. That of nickel, on the other hand, evidently is not accompanied by a heat effect as Shukoff found no retardation (differential method) between 600° and 180°C.[1]

The effect of the field strength on the magnetic transformation of pure iron is very marked. For low field strengths the magnetism increases slowly up to the transformation point. At this temperature it suddenly rises to a sharp maximum and then drops off to nearly zero, whereupon the iron becomes weakly magnetic. As the field strength increases, the maximum decreases in absolute value and shifts to lower temperatures, until it finally disappears. In higher field strengths, between 50 and 100 gausses, the transformation takes place over a considerable range in temperature, about 250°C. This phenomenon is in apparent disagreement with the phase rule, according to which the transformation of one phase of iron into another should take place at constant tempera-

[1] *Journ.* Russk. Fisik-Chimices k. Obs., 1908, Vol. 40, p. 1748.

ture. According to the latest ideas, however, these two forms of iron are not distinct phases in the sense of the phase rule, and, therefore, an "equilibrium" temperature need not be considered. In other words, the change of ferromagnetism to para-magnetism in magnetic substances on heating is a "temperature" effect, probably atomic in character, as contrasted with "phasial" phenomena.

The specific susceptibility of silicon, arsenic, selenium, diamond, crystallized boron, vanadium, molybdenum, tungsten, copper, sulphur, and osmium were found by Honda to be nearly independent of the temperature, at least up to 1100°C. At the melting points the specific susceptibility either passes through a discontinuity, through a transition point, or does not change at all. The mesals featured by a sharp discontinuity at the melting point are bismuth, silver, lead, gold, tellurium, antimony, tin, phosphorus, and thallium, while transitions at the melting points are noted on the curves of aluminum, iodine, sodium, and cadmium. The melting points of magnesium, selenium, zinc, sulphur, potassium and indium are passed through without causing any change in the specific susceptibility. In these cases there would be a change in κ (as distinguished from specific susceptibility), which would be due to the change in volume on the change of state.

Transformation points in the elements, similar to the melting points, are at times brought out on the curves, at times not. The transformation point of thallium at 230° is shown by a discontinuity while that of zinc at 300° is somewhat poorly shown by a transition. The transformations of tin, silicon and titanium are not brought out by this method.[1]

Magnetic Properties of Binary Alloys.—Here again, in order to secure measurements of the magnetic properties which are truly representative of the materials, themselves, *i.e.*, to eliminate differences due to differences in density, the specific susceptibility is plotted as a function of the composition. Strictly speaking, in order to obtain accurate measurements, the field within the specimen must be homogeneous. This would be true only in case the test bar were in the form of an ellipsoid, and structurally homogeneous. It is evident that this condition is not satisfied in the case of the metals as they are always aggregates of crystals varying in orientation from crystal to crystal. This

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[1] HONDA, *loc. cit.*

condition is departed from still further, in the present case, as binary alloys are very often non-homogeneous solid solutions or even mechanical mixtures.

In considering the magnetic properties of a mixture of two phases, one ferromagnetic and the other weakly magnetic, the demagnetization due to the field established by the magnetic substance plays an effective part in determining the shape of the curve of magnetization vs. concentration. The effective density of the field acting on the interior of the heterogeneous mixture, is given by the external field decreased by the algebraic sum of the demagnetizing effects of the ferro- and non-ferromagnetic substances. For a given external field this demagnetizing effect increases as the number of polyhedrons of a given size per unit volume decreases, so that the magnetization decreases at a more rapid rate with decrease in the number of ferromagnetic grains per unit volume, than would be expected from the mere decrease in number. From this it is evident that the variation in magnetism over a range in concentration corresponding to a heterogeneous mixture of two phases, one ferro- and the other non-ferromagnetic, will not be linear with the concentration. Even so, it is clear that if the test bars are magnetically saturated, the function will be strictly linear.

In alloys in which both phases are weakly magnetic, in which case the demagnetization is negligible, the magnetic properties are regular functions of the concentration.

The variation in magnetism over a series of solid solutions does not follow any definite law and must be determined experimentally in each case. One general rule is given that an alloy of a ferromagnetic metal and a relatively small amount of a non-ferromagnetic metal, is ferromagnetic, but it cannot be told in advance whether the magnetism will be greater or less than that of the ferromagnetic metal. The addition of chromium to nickel decreases the magnetism as a linear function of the composition by weight, until, at 10 per cent. chromium, the value of I has dropped to zero. The addition of 15 per cent. chromium to cobalt, on the other hand, increases the magnetism. More than this amount of chromium causes the magnetism to drop off suddenly, until at 25 per cent. chromium it becomes practically zero. Nickel, even though a magnetic metal itself, robs iron of its magnetism when about 27 per cent. to 35 per cent. are present. The decrease is a linear function of the

concentration. Even the non-magnetic iron-nickel alloys, when cooled to $-100°$C., become magnetic, which magnetism they retain until heated above $400°$C., so that it is possible to obtain these alloys in either a magnetic or a non-magnetic state at room temperature. The addition of more than 35 per cent. nickel restores the ferromagnetism. In general, however, the alloys of the ferromagnetic metals among each other are magnetic throughout.

Honda has also made a study of the effect of second metals on the transition temperatures of the ferromagnetic metals. This effect is well illustrated by the chromium-nickel alloys. The magnetic transformation of nickel lies at $350°$C. and it is at the same temperature on heating and on cooling. The addition of 2 per cent. of chromium lowers the temperature of the transformation and causes it to take place over an interval of temperature; viz., $240°$-$280°$ on heating. Furthermore, the transformation takes place at lower temperatures on cooling than on heating, the difference being about $15°$. Hill[1] has shown that the depression of the transformation temperature of nickel by copper and tin can be calculated from the van't Hoff formula for the molecular depression of the freezing point.

$$\Delta t = 0.02 \ mT^2/ML$$

Compounds of ferromagnetic metals with other metals are not ferromagnetic as a rule, while, on the other hand, compounds of the ferromagnetic metals with the metalloids, especially those compounds containing the greatest amount of the ferromagnetic metals, are ferromagnetic. The compounds FeO, Fe_3O_4, Fe_2O_3, and FeS are ferromagnetic; Fe_3P, Fe_2P, and Fe_3C are moderately magnetic, and Fe_3Sb_2 is weakly magnetic. The compounds of the other two ferromagnetic metals, cobalt and nickel, have not been thoroughly enough examined to permit making a general statement. Co_4S_3 and Ni_3S_2 can be magnetized while FeS_2, NiO and NiS are hardly ferromagnetic.

For reasons stated above, the relationship between the susceptibility of the weakly magnetic alloys and the concentration is much simpler than that for ferromagnetic alloys. The function is linear over those compositions in which the alloys consist of two phases and is, therefore, represented by a straight line. If intermetallic compounds are present, these lines intersect at the

[1] *Verh.* deuts.phys. Gesell., 1902, Vol. 4, p. 194.

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compositions of the compounds. The specific susceptibility of solid solutions is also a linear function of the composition, as the magnetic properties are independent of the crystalline structure. This is verified by the nickel-tin and the nickel-aluminum alloys which lie toward the nickel end and at temperatures above 550°C.

The Heusler Alloys.—Heusler made the discovery, in 1903, that manganese and certain other weakly magnetic (paramagnetic)[1] metals, when combined, produce ferromagnetic alloys. The base of these alloys was usually an alloy of manganese and copper, rich in copper, to which were added various amounts of antimony, arsenic, tin, aluminum and bismuth. As a simple illustration of the Heusler alloys can be taken the Mn-Sb alloys which were examined by Honda.[2] According to Williams[3] the structure of the manganese-antimony alloys is as follows:

Composition	Structure
0.3 to 31.2 per cent. Mn	Sb + saturated solid solution with 31.2 per cent. Mn.
31.2 to 40.7 per cent. Mn	Solid solutions of Mn_3Sb_2 with Sb.
40.7 to 47.8 per cent. Mn	Mixtures of two saturated solid solutions.
47.8 to 50.5 per cent. Mn	Solid solutions of the compound Mn_2Sb with Mn.
50.5 to 100 per cent. Mn	Solid solutions with 50.5 per cent. Mn + Mn.

Fig. 85 represents the variation in magnetism of the manganese-antimony alloys. The curve has two maxima and one minimum. As has already been pointed out, the magnetization of a series of strongly magnetic solid solutions can vary according to any type of curve, and in this series the greatest magnetization comes, not at the composition of the compound Mn_3Sb_3, but at the composition corresponding to the saturation point of Sb in this compound. The same is true of the series Mn_2Sb-Mn; the second maximum corresponds to the saturation point of Mn in Mn_2Sb. The alloys of manganese and aluminum are somewhat analogous and contain the compounds Mn_3Al and $MnAl_3$. The compound Mn_3Al is noticeably magnetic, while copper, which goes into solution in this compound, produces alloys which are quite strongly magnetic.

[1] Ihde and others have shown that manganese exhibits ferromagnetism so that, strictly speaking, it cannot be classed as a non-magnetic metal. *Ann. Physik*, 1913, Vol. 41, 4, p. 829.

[2] *Loc. cit.*

[3] *Zeits*. anorg. Chemie, 1907, Vol. 55, p. 1.

These two cases illustrate the essential characteristics of the Heusler alloys, viz., they are alloys which contain an intermetallic compound with another substance (one of its own elements or a third element) in solid solution.[1] It is, of course, possible that a ternary compound is formed with the third metal which in turn forms a series of solid solutions with the binary compound.

The Heusler alloys behave as all other ferromagnetic substances when heated, as each one has a definite temperature, or temperature interval, at which it loses its property of being strongly magnetic. The variation of magnetic properties of the Heusler alloys with the field strength has not been followed.[2]
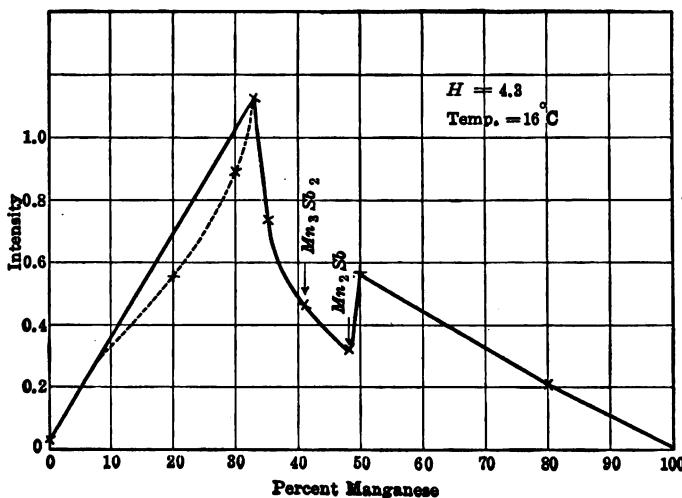
Fig. 85.—Magnetism of the manganese-antimony alloys. (*Honda.*)

The general rules regarding the magnetic properties and the constitution of alloys, as laid down by Tammann[3] and confirmed by the work of Honda, are:

[1] The effect of the stoichiometrical relationship of the compound on the magnetic properties, as is given by Wedekind for chemical compounds, is not clear; at least no such relationship has been established as yet. (WEDEKIND, "Relations between the Magnetism and the Stoichiometrical Constitution of Chemical Compounds," *Met. & Chem. Eng.*, 1912, Vol. 10, p. 402.)

[2] For information on the Heusler Alloys, see GUTHE and AUSTIN, *Bull. Bureau of Standards, Reprint* No. 38; Ross and GRAY, *Proc. Roy. Soc. of Edinburgh*, Vol. 31, p. 85; Ross, *Journ. Inst. Met.*, 1910, No. 2, p. 68.

[3] *Zeits.* Phys. Chem., 1909, Vol. 65, p. 73.

1. The ferromagnetism of alloys is confined to a definite phase, for change of both the temperature and chemical composition.

2. The addition of a non-ferromagnetic metal to a ferromagnetic metal, if it forms a series of solid solutions, can cause either an increase or a decrease in the magnetism.

3. Magnetization in a series of alloys composed of two phases, only one of which or both of which are magnetic, is a linear function of the total composition, in as far as the reciprocal action of these two phases (demagnetization) does not interfere.

4. It follows that the magnetization of weakly magnetic alloys varies as a linear function of the concentration.

Electrolytic Potential.—If a metal is dipped into a dilute aqueous solution of a salt of that metal, an electromotive force is established which, at any temperature, depends upon the solution pressure of the metal and the concentration of the metal ions in the electrolyte. Thus, according to Nernst's formula

$$e = \frac{RT}{nF} \log \frac{P}{p}$$

where R is the gas constant, T is the absolute temperature, n is the valence of the metal ions, F is one Faraday, P is the electrolytic solution pressure of the metal, and p is the osmotic pressure of the ions in the electrolyte.

This is the property which has been used somewhat the same as the electrical conductivity, specific volume, etc., as a means of studying the constitution of metallic alloys.

The zero of potential is taken as the potential of the more electropositive metal of the series, measured in an electrolyte of a salt of that metal. The measurements of a series of alloys are then made by determining the e.m.f.s of a series of cells of the general form

more positive metal/electrolyte/alloy.

The electrolyte must contain metallic ions of the two metals and be of such composition that it will be in equilibrium with the alloy. Aqueous solutions of salts of the two metals, or fused salts of the two metals are used in this work.

If the cell is not subject to polarization, the e.m.f. can be measured directly by means of a voltmeter, preferably one which has a comparatively high resistance, above 100 ohms. If it is necessary to reduce the e.m.f. of the cell in order to measure it with the apparatus on hand, a standard cell can be used in opposition

to it so that the measurement is actually the difference between the two e.m.f.'s

The most common as well as the most accurate method employed at present is the compensation (potentiometric) method of Poggendorff. This method is especially useful for measuring the e.m.f.'s of cells which polarize. The principle of the method briefly stated, is that a known e.m.f., which can be varied and measured at all times, is introduced into the circuit in opposition to the e.m.f. of the cell. The known e.m.f. is then varied until no current flows, as determined by a highly sensitive galvanometer. The measurement made in this way eliminates polarization and is independent of the internal resistance of the cell and the galvanometer.[1] During the initial compensation of the two e.m.f.'s a large resistance of from 1000 to 100,000 ohms is used to prevent polarization by taking off current from the cell. During the fine adjustment this resistance is short circuited.

In many determinations the sensitive galvanometer is replaced by a capillary electrometer.[2] The capillary electrometer has one advantage over the zero point galvanometer, in these determinations, in that it is sensitive to differences in potential and not to the amount of current flowing.[3]

The e.m.f., E, of the cell is composed of e_1 the potential between the pure metal and the electrolyte, and e_2 the potential between the alloy and the electrolyte; i.e., $E = e_1 - e_2$. e_1 depends both on the nature of the metal and on the ionic concentration of the electrolyte while e_2 depends upon the composition of the alloy and the ionic concentrations of the two metals in the electrolyte. E is the quantity measured and is the one which is used in the investigation of the constitution of metallic alloys.

If the electrolytic potential were as simple to determine as various other physical properties, it would undoubtedly be more extensively used, chiefly because the results are capable of direct interpretation in terms of the constitution. Among the factors which interfere with these measurements may be mentioned the following:

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[1] The details of this method are given in ALLMAND, p. 90. See also "Handbuch der Arbeitsmethoden i.d. anorganischen Chemie," Vol. 3, Pt. 2, p. 885.

[2] See OSTWALD and LUTHER, "Lehrbuch," 3d Ed., 1910, p. 430.

[3] For the preparation of electrodes see "Handbuch der Arbeitsmethoden" and OSTWALD and LUTHER, "Lehrbuch der Allgemeinen Chemie."

1. It is difficult to secure an electrolyte which is in equilibrium with the alloy. Any other electrolyte will cause a variation in composition at the surface of the alloy so that the results obtained will apply in reality to another alloy rather than the one under observation. The proper ionic ratio of the electrolyte for use with alloys which form solid solutions should be determined by preliminary experiments, as Tammann suggests,[1] by noting the effect of varying the ionic concentration on the alloy. To do this, the ionic concentration of the more noble metal should be increased until the solid solution of the more noble metal is no longer precipitated out of the electrolyte, and if possible, until the less noble metal begins to separate from the solid solution.

2. If the alloy is composed of two or more phases, secondary local action can take place which may not only affect the character of the surface of the alloy, but which may also give rise to changes in the observed potential.

Due to the neglect of these factors much of the work which has been done in the past has given erroneous results.[2]

The relationship between the electrolytic potential and the physical constitution of binary alloys was first given by Reinders.[3] In this treatise Reinders pointed out the necessity of having

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[1] TAMMANN, "Lehrbuch der Metallographie," 1914, p. 339.

[2] For the details of the principal work which has been done so far in this field, reference should be made to the following: TROWBRIDGE and STEVENS, *Proc.* Amer. Acad. Arts & Science, 1882–3, p. 221. This work is interesting in that it is probably the first to indicate the succession of phases in the Cu-Zn system, although it was incorrectly concluded at the time that the e.m.f. varied as the metal which was most readily dissolved by the electrolyte.

A. P. LAURIE, *Trans.* Chem. Soc., 1888, Vol. 53, p. 104; 1889, Vol. 55, p. 677; 1894, Vol. 65, p. 1031; *Phil. Mag.*, 1892 (5) Vol. 33, p. 94; *Zeit.* phys. Chem., 1909, Vol. 67, p. 627.

M. HERSCHKOWITSCH, *Zeit.* phys. Chem., 1898, Vol. 47, p. 123.

W. REINDERS, *Zeit.* phys. Chem., 1902, Vol. 42, p. 225.

N. A. PUSCHIN, *Zeit.* anorg. Chemie, 1907, Vol. 56, p. 1. In this article are the determinations of the e.m.f. curves of fourteen series of binary alloys. This work is open to the criticism that the electrolytes used were either solutions of salts of the more positive metal or of sulphuric acid.

KREMAN and HOFNEIER, "Electromotive Force of Ternary Alloys," *Monatshefte f. Chemie*, 1911, Vol. 32, p. 597.

For the theoretical considerations involved, see ALLMAND, "Applied Electro-chemistry," 1912, and NERNST, "Theoretical Chemistry."

[3] For the periodicity of the e.m.f.'s of the elements, see PALMAER, NERNST's "Festschrift," 1913, p. 332.

chemical equilibrium at the surface of contact between the alloys and the electrolyte, a condition which was not secured by Laurie and Herschkowitsch who used as electrolytes aqueous solutions of sodium chloride and of the more positive metal, respectively.[1]

On the basis of the phase rule, Reinders gave the relationship between E and the composition for the following cases.

Case I. The two metals are insoluble in all proportions. The potential of a reversible electrode has already been stated. To establish the relative ionic concentrations of the two metal ions
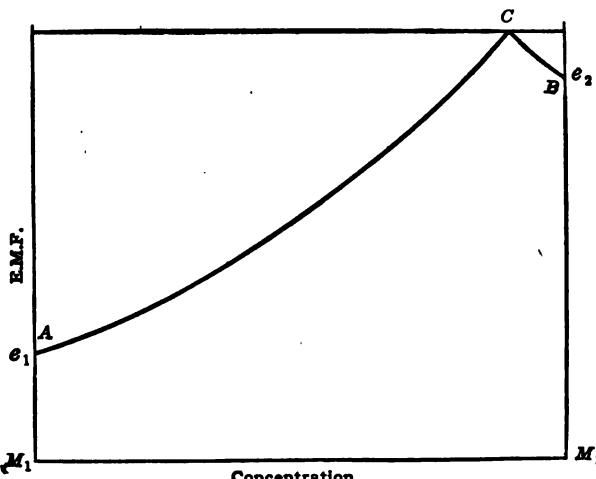
Fig. 86.—Electrolytic potential curves: the metals M_1 and M_2 are insoluble in each other.

in the electrolyte with which both metals are in equilibrium, we may proceed somewhat as follows. The ionic concentration of M_1 and M_2 may be expressed as

$$\frac{C_{M2}}{C_{M1}+C_{M2}}, \text{ where } C_{M1} + C_{M2} \text{ remains constant.}$$

The electrolyte in this case may be either an aqueous solution or a fused mixture of salts of the two metals. If part of the ions of the metal M_1 are replaced by ions of the metal M_2, the osmotic pressure of the M_1 ions decreases so that e_1 increases. The same would be true of the reversible electrode of the second metal M_2 by the addition of M_1 to the electrolyte. The change of potential produced by varying the composition of the electrolyte, is given by two (logarithmic) curves which intersect at a

[1] See also, Nernst, *Zeit.* phys. Chem., 1897, Vol. 22, p. 539.

point C, Fig. 86. The point C gives the equilibrium potential of the two metals in the electrolyte as a function of their ionic concentrations in the electrolyte, the total concentration of which, it must be remembered, remains constant for all compositions from M_1 to M_2. It is the composition C and only this composition which is in electrolytic equilibrium with both of the metals. All other electrolytes of the series are in equilibrium with only one of the metals. An increase in the total ionic concentration $(C_{M1} + C_{M2})$ shifts the curve towards lower potentials and, vice versa, a decrease shifts the curve towards higher potentials. For the potential C, $e_1 = e_2$ and it can be
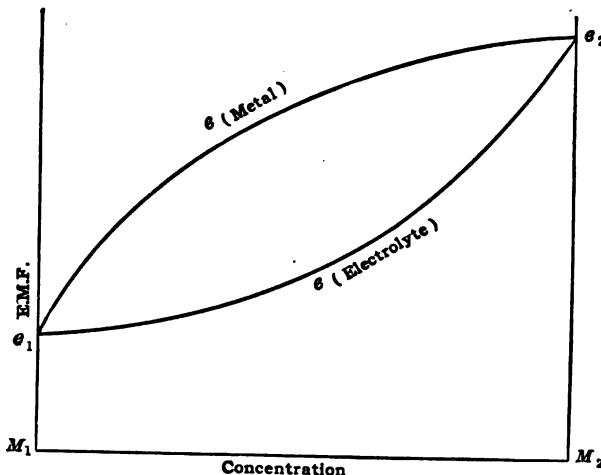
FIG. 87.—Electrolytic potential curves: the metals M_1 and M_2 are soluble in all proportions.

shown that $P_a : P_b :: p_a : p_b$, when $n_1 = n_2$, or the electrolytic solution pressures of the metals are to each other as the concentrations of their ions in the electrolyte. As the solution pressures of the two metals will be quite different, in general, it follows that C must lie close to one of the pure metals.

If the potentials of a series of alloys of A and B are measured against A, in a solution of the composition corresponding to the point C, the equilibrium tension of all these alloys will be the same ; *i.e.*, the tension corresponding to C. Experimentally, this potential will be that of the less noble metal B for all compositions except those compositions of the series close to A. In these, if the eutectic is present in such a small amount that it

does not come in contact with the electrolyte, the potential will sink to the value of pure A or zero. If a value is found which lies intermediate between those of the two pure metals, it can be due to the experimental error of taking off too much current, or if this is eliminated, to a slight solubility of B in A.

Case II. The two metals form homogeneous solid solutions. In this case the electrolytic potential varies continuously from one pure metal to the other. The upper line in Fig. 87 gives the variation of potential with the composition of the alloy, which is rapid with the first additions of the less noble metal. The
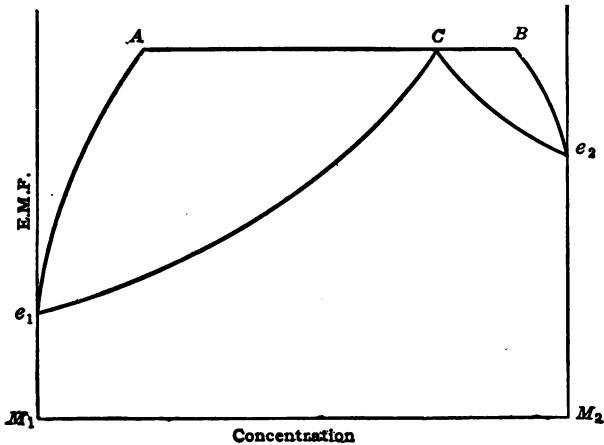
FIG. 88.—Electrolytic potential curves: the two metals M_1 and M_2 are partially soluble in each other.

lower line gives the variation of the potential with the ionic ratio of the electrolyte which is in equilibrium with the alloy. The ratio of the amounts of A and B in the alloy and in the electrolyte will, in general, be different so that these two lines will not coincide.

Reasoning with the phase rule as a basis, Reinders arrived at the conclusion that the system is monovariant so that the ratios of the two metals in the solid solutions and the two metallic ions in the electrolyte can be varied and still maintain equilibrium, but that any particular solid solution will be in equilibrium with only one electrolyte. This shows that the difference in potential between the alloy and the electrolyte varies with the concentration. If the two components vary but slightly in their electrolytic solution pressures, a maximum or a minimum is possible on the curve in Fig. 87.

Case III. The two metals are partly soluble in each other. In this case, the two saturated solutions are in equilibrium with an electrolyte of a definite composition; that is, the potential measured against this electrolyte is the same for both of the metal phases. If this potential is larger than either of the pure metals, we get the curve in Fig. 88, whereas if it is intermediate in value we get the curve in Fig. 89.
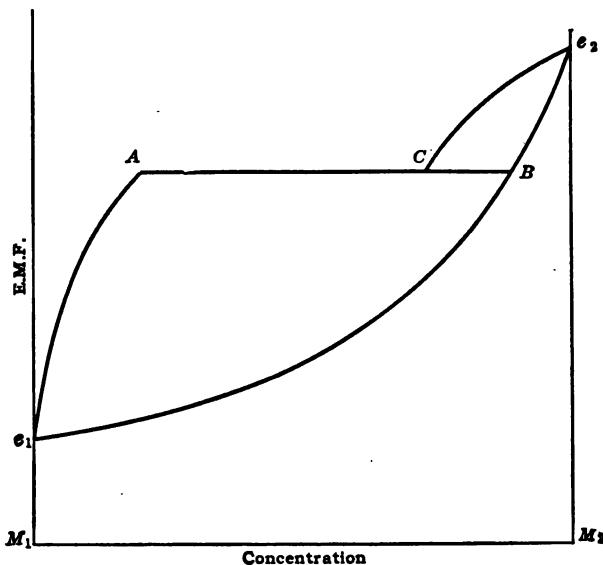

Fig. 89.—Electrolytic potential curves: the two metals M_1 and M_2 are partially soluble in each other.

Case IV. The two metals form an intermetallic compound. By assuming that the compound, as an electrode, gives off ions of the same composition, the diagram can be divided into two parts as in Fig. 90. Assuming insolubility in the solid state, the potential remains constant between the two pure metals and the compound. A sudden change at the compound signifies the presence of such a compound. If the change is a gradual one at this point, or at the other ends of the two series, and if it were known that this is not due to the failure of exposing the eutectic to the electrolyte, a certain solubility in the solid state would be correctly assumed. If there are several intermetallic compounds present, there will be as many abrupt changes in the potential, as just described; but it must be remembered that the variation

in the electrolyte potential as just given, and based upon Nernst's formula, assumes that the electrolyte chosen is such a one that it will be in equilibrium with the alloy.[1]
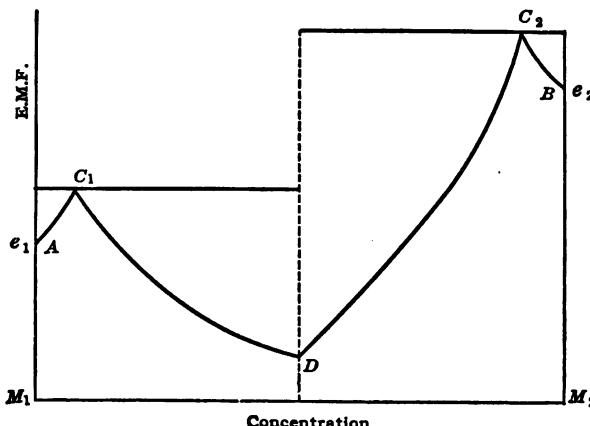

Fig. 90.—Electrolytic potential curves: the two metals M_1 and M_2 form a compound.

The Effect of Stress and Mechanical Work.—It has been shown, by various experimenters, that a stress applied to a metal or alloy makes it more electropositive; but there is as yet very poor agreement among the results obtained and between the theoretical increase, which is calculated on the assumption that the increase in potential is proportional to the change in free energy, and the increase found experimentally. This change in potential was shown, at least qualitatively, at an early date by Hambuchen[2] who experimented with iron. Walker and Dill[3] found that when soft iron is strained in a testing machine below its elastic limit, the potential drops by about 0.0001 volt, which may be explained as being due to drop in temperature of the test bar on being deformed. Richards and Behr[4] have shown that the change produced by straining iron below the elastic limit, is very small and quite variable. When the stress applied was above the elastic

[1] For a brief summary of the application of this method to the investigation of intermetallic compounds, see DESCH, "Intermetallic Compounds," 1914, p. 60.

[2] *Bull.* Univ. Wisconsin, 1900, No. 8.

[3] *Trans.* Amer. Electrochem. Soc., 1907, Vol. 11, p. 153.

[4] Carnegie Institute, Washington, 1906, No. 61.

limit, they found a sudden increase of several hundredths of a volt, which was governed largely by the rate of strain. Mercia[1] has shown that the e.m.f. of brass in a solution containing both copper and zinc ions is increased by about 0.2 mv. for a stress of 20,000 pounds per square inch and about 1 mv. for 30,000 pounds per square inch at the yield point, the mesurements being made against an unstressed bar of the same material.

Spring found in 1902, that cold deformed metals, such as tin, lead, cadmium and silver, become the anode when placed in an electrolyte and measured against the annealed metal. The difference of potential found was from 0.1 to 0.2 mv. Strained bismuth, on the other hand, became the kathode, showing a difference of potential of -3.85 mv.[2] In the same way it was found by Fawsitt[3] that rolled or hammered copper becomes the anode when compared with annealed copper.[4]

Two silver rods, after having been annealed for several hours, showed no difference in potential when placed in an electrolyte of silver nitrate. One of the rods was then polished with emery paper and again inserted. This time the cell showed an e.m.f., the polished rod being the negative pole, and differing in potential from the positive rod by 0.013 volt. By either treating the polished rod with nitric acid and warming to about 200° or by heating it to a red heat, the e.m.f. disappeared. This same phenomenon was verified with gold and platinum. According to this it is essential to have the electrodes in a known state before measuring the potential.

Cohen and van Eijk have used the electrolytic potential to determine the transformation point of pure tin.[5] They used an H-shaped flask containing gray tin in both sides in a 10 per cent. solution of tin-ammonium chloride. One side was dipped in warm water to convert the gray tin into white tin, which action immediately produced a difference in potential. The entire flask was then cooled to below the transformation point, and, as the

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[1] *Technologic Paper*, Bureau of Standards, 1916, No. 83.

[2] *Bull*. Acad. Belg., 1902, No. 12, p. 1066.

[3] *Proc*. Royal Soc. of Edinburgh, 1905–06, Vol. 26, p. 2.

[4] It has been shown by WIEDMANN ("Electrizität," Vol. 1, p. 723) that liquid gallium is electropositive to solid gallium in gallium sulphate, and it has been inferred from this that plastic deformation gives rise to a small amount of the liquid amorphous phase in metals.

[5] "Physico-Chemical Studies of Tin," *Zeit*. phys. Chem., 1899, Vol. 30, p. 601; 1900, Vol. 33, p. 57; 1900, Vol. 35, p. 588.

change from white to gray tin is very sluggish, there was still essentially the same difference in potential. On gradually raising the temperature again the gray tin changed to white tin at the transformation temperature as was indicated by he disappearance of the potential. The temperature found was 20°C.

Electrolytic Precipitation of Metals and Alloys.—It can be seen from the diagram in Fig. 86 what the effect is of passing a current through an electrolyte. The metal phase which is in equilibrium with the electrolyte will be precipitated if the potential of the cathode is made greater than the potential of the metal against the electrolyte. In this way the pure metal A will be separated out of electrolytes whose compositions are given by the line A-C in Fig. 86. A and B can be precipitated simultaneously out of the electrolyte of composition C in the ratio in which they exist in the electrolyte. By keeping the composition of the electrolyte richer in A than the amount given by point C, a separation of the two pure metals A and B can be effected.

The principles governing the electrolytic deposition of alloys have been laid down and tested by Kremann and his collaborators.[1] They have shown the relations between the potentials required to produce hydrogen, or the metal, or both; and further, that in order to precipitate the two metals simultaneously as a solid solution, the individual potentials of both metals and the electrolyte must be equal, otherwise that metal will be first deposited on electrolysis whose potential is lower toward the salt solution, *i.e.*, the one which is more electro-negative.[2] Applying this to the precipitation of brass from a double sulphate solution of zinc and copper, it was shown that the copper must be made more positive in order to make its potential approach the potential of zinc toward zinc sulphate. To do this, KCN was added to the electrolyte to form complex ions with the copper and thus reduce the osmotic pressure by diminishing the concentration of the simple copper ions. But even though the potentials of zinc and copper were made equal in this manner, brass was not precipitated, due to the fact that a correction for the solution pressures of the metals on forming a solid solution, must be made. The precipitation was obtained when the potentials of zinc and

[1] KREMANN, SUCHY and MAAS, *Monat. Chem.*, 1913, Vol. 34, p. 1757; KREMANN, LORBER and MAAS, *Monat. Chem.*, 1914, Vol. 35, p. 581.

[2] For example: Cu would be first precipitated out of a zinc-copper sulphate solution by electrolysis.

copper were 0.4 volt different.[1] In this way the more noble
metal is able to assist in the electrolytic deposition. Another
condition which must be fulfilled is that the electrolyte must
remain constant and uniform in its composition. In other words,
the concentration of the metallic ions must remain unchanged
at the cathode.

These experiments have been continued on nickel-iron and
other alloys, but as yet the difficulties encountered are too great
to permit of any general application of this method to the prepara-
tion of metallic alloys.

Curry[2] has prepared copper-tin alloys by electrolytic deposi-
tion and has shown that the alloys can be deposited under condi-
tions of stable equilibrium; *i.e.*, the succession of the phases and
their ranges in composition are the same as in alloys prepared
by the thermal means and stabilized by long annealing. Greater
difficulty has been encountered on attempting to prepare alloys
of copper and zinc.[3]

Bruni and Amadori[4] studied the electro-deposition of copper-
nickel, iron-nickel, iron-cobalt and nickel-cobalt alloys and the
relation between the composition of the deposit and the current
density and voltage.

Field,[5] in his work on the deposition of silver-copper alloys,
determined the limits of composition of the electrolyte between
which both metals are deposited simultaneously.

A great amount of additional work has been done on the elec-
trolytic deposition of metals and alloys but it possesses less
interest for the metallographist than for the electro-chemist
and the subject will not be considered further here.

Thermo-electric Force.—The principle of thermal electro-
motive force has already been briefly stated; viz., that if two
unlike substances are in contact at a point which is at a different
temperature from the free ends, the free ends will generally be at
different potentials. The difference in potential depends chiefly

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[1] For the effect of alloying on the e.m.f. see, for example, A. COHEN, *Zeit.*
phys. Chem., 1901, Vol. 38, p. 609.

[2] *Journ.* Phys. Chem., 1906, Vol. 10, p. 515.

[3] The electro-deposition of brass has been very systematically investigated
by BENNETT and DAVISON, *Trans.* Amer. Electrochem. Soc., 1914, Vol. 25,
p. 347.

[4] *Atti della R. Accad. Padova*, 1913–1914, Vol. 3, p. 349 and *Ann. di Chem.
Appl.*, 1915, Vol. 3, p. 147.

[5] *Trans.* Faraday Soc., 1910, Vol. 6, p. 1.

upon the difference in temperature, and, of course, the nature of the two substances. The introduction of a third material between the points of contact at the hot junction, such as a solder, has no effect on the electromotive force provided no variation in temperature is caused thereby. According to the theory of Kohlrousch and Liebenow, a wire heated to different temperatures along its length will be at different potentials, the difference in potential being due to the difference in temperature, and depending on the thermal conductivity. The e.m.f. for one degree Centigrade difference in temperature, can be expressed as

$$e = H = \pm 2.04 \sqrt{RL/r}$$

in which R is the electrical resistance of the metal in ohms, L is the thermal conductivity in gram calories per second, and r is the absolute temperature of the hot end.[1] .Two different metals, having different thermal conductivities, will have different thermo-electric forces and a couple of the two metals will show an e.m.f. which is equal to the difference between the two e.m.f.'s of the two metals. It appears that in all metals, the hot end is positive (in non-metals negative) so we can make use of only the difference in the e.m.f.'s and never the sum. However, the previous treatment of the material has a decided influence and its effects should always be eliminated as far as possible, by annealing, before taking measurements. Impurities in either of the elements of the thermo-couple always influence the thermo-electric force as we shall see later.

Another point which must be considered at times, is the variation in the thermal electromotive force with the crystallographic orientation so that different values are obtained according to whether the flow of heat or electricity is parallel with one axis or with another. Among the metals this is particularly noticeable with bismuth, antimony and tellurium, which crystallize in the rhombohedral form. When a cast bar or rod is used to determine the thermoelectric force, the value obtained is always a mean value depending upon the orientation of the individual crystals. This of course, may or may not be the source of an appreciable error.

The e.m.f. of the thermocouple, expressed as a function of the temperature, is given by the equation $E = f(t)$. By differentiating with respect to the temperature we get a quantity dE/dt,

[1] See LIEBENOW, *Elektrotech. Zeit.*, 1900, Vol. 21, p. 246.

which is designated by *H*, and which is called the "thermo-electric force." This quantity is the one which is used to compare the behavior of different metals and alloys. The elements of the couple used are wires of the different metals, in case the materials can be drawn. One of the wires is the alloy tested, and the other is either one of the pure metals of the series, or else a neutral wire such as copper or platinum. If the material cannot be drawn into wire, cast rods are used. The electromotive force developed by the couple is measured either by a deflection galvanometer or by the potentiometer, both of which have already been described.

It has thus far been impossible to obtain any one formula which will express the relation between the temperature and thermal electromotive force of all metal or alloy pairs. The formulae which are used are empirical, and each one applies only to an individual type of couple or over a limited range in temperature. Several of these formulae have already been given. *H* is a linear function of *t* for most of the common couples; but for metals such as iron and lead it varies considerably, even changing sign, and passing through maxima and minima.[1]

Allotropic transformation points of pure metals and even melting points can be located by determining the variation in thermoelectric force over a wide range in temperature, using copper or platinum as the neutral element. At the transformation point, the thermoelectric force changes abruptly. Siebel has measured the change in *H* at the melting points of mercury, sodium, bismuth, tin, antimony, lead, the binary system bismuth-tin, and the ternary system bismuth-tin-lead.[2]

Thermoelectric Force and Composition.—The variation of the thermoelectric force with chemical composition follows the same laws that were given above for electrical conductivity and thermal conductivity. Recapitulating, we may state that the thermoelectric force varies as a linear function of the composition, if the alloys consist of heterogeneous mixtures and according to the well-known U-shaped curve, if they form a series of solid

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In potentiometer construction it is desirable to use a metal with manganin, the resistor, with a low *H*. This has been discussed by WARREN and MURPHY, *Electrician*, 1908, Vol. 60, p. 602; and JOLLEY, *ibid.*, p. 608, who considered the relative merits of copper and phosphor bronze.

[2] SIEBEL, *Ann. Physik.*, 1914, Vol. 45, p. 839. For discussion of this point see KOENIGSBERGER, *Ann. Physik.*, 1915, Vol. 47, 4, p. 563.

solutions. An intermetallic compound is brought out by a cusp pointing upwards.[1] In the case of those alloys, whose thermo-electric force varies with the crystallographic orientation, (alloys of bismuth with cadmium and antimony with tellurium) measurements of the thermoelectric force can lead to fallacious conclusions regarding the constitution.

The Effect of Strain.—The effect of strain on the thermo-electric force has been investigated for nickel and other metals by M'Whan.[2] The couple was made of two wires of the same metal, one of which was stressed; one junction was at 100°C. and the other at room temperature. The effect of increasing the stress on the e.m.f. was determined, and was found to be represented by a straight line for nearly all the metals tested.[3]

Commercial Applications.—The chief commercial application of thermocouples is to the measurement of high temperatures in the chemical and metallurgical industries. This subject has been discussed in Chapter V.

[1] HAKEN, *Ann. Physik.*, 1910, Vol. 32, p. 291.

For a theoretical consideration of the thermal e.m.f. of alloys and its expression in terms of the ratio of the electrical and thermal conductivities, see BERNOULLI, *Ann. Physik.*, 1910, Vol. 33, p. 690.

For the thermoelectric force of Au-Ag, Cu-Ni, Bi-Sb, Ag-Pt, Ag-Pb, Pt-Rh, Pt-Ir, steels, Bi-Pb, Bi-Cd, Bi-Sn, Cu-Co, Cd-Sb, and Cu-Al, as well as a theoretical discussion of the thermoelectric properties of alloys, see BRONIEWSKY, *Rev. Metal*, 1910, Vol. 7, p. 341; *Comptes Rendus*, 1909, Vol. 149, p. 853; see also DANNECKER, *Ann. Physik*, 1913, Vol. 43, p. 1504, for the thermoelectric properties of many of the common couples.

For a general discussion of the thermal electricity of the alloys, see RUDOLFI, *Zeit.* anorg. Chemie, 1910, Vol. 67, p. 65.

[2] *Proc.* Royal Soc. of Edinburgh, 1913–14, Vol. 34, p. 64.

[3] The effect of strain on the thermoelectric behavior of metals and alloys has also been reported on by MACLEAN, Royal Soc., *Proc.*, 1900, Vol. 66, p., 165. Among other things, he noted a change in sign of the e.m.f. as the permanent deformation increased above a certain amount.

THE MECHANICAL PROPERTIES OF METALS AND ALLOYS

Mechanical Testing.—The mechanical properties of metals and alloys are determined less for the study of the constitution, which they afford, than for the direct information which such determinations give as to the quality of the material tested, the influence of heat and mechanical treatment, chemical composition, etc., and the probable behavior of the material in service. These tests are carried out in the experimental laboratory and are intended to supply information for use in the selection of materials for engineering purposes and the treatments they should receive prior to their being placed in service. These tests are then followed by "acceptance tests" of the finished material as a means of determining if the requirements have been met. There are two basic principles underlying these tests which have been very aptly stated by Rosenhain. One is that the test in the laboratory should duplicate or correspond as closely as possible to the service conditions. There is the difficulty here, that service conditions can rarely be strictly simulated in the laboratory so that the best that can be obtained is a correlation of the experimental test of the material, with its actual behavior. This requires the accumulated experience of numerous engineers over a period of years and the final judgment of the material, at the best, is arrived at in a most laborious fashion. The second principle is that each test should be so conducted as to bring out some one property or at the most some simple combination of properties which can be readily analyzed, and eliminate, as far as possible, other effects. The successful use of the second principle rests upon a searching analysis, on a sound scientific basis, both of the service conditions and of the properties which the materials must possess, adequately to meet the requirements. This is the present trend in the testing of materials and the principle, as it is commonly applied, is fundamentally sound although the actual behavior in service is necessarily the final test. Before leaving this point it should be stated

that, apparently, the second principle has failed in many cases to give the true index of the probable behavior of a material in service and that therefore the tests should be of the first kind. On second thought, however, it seems as if the analysis of the problem has been inadequate and that the failure was due to insufficiency in some property which was not tested. Certain cases indicating the truth of this will be cited later on.

To the metallographist, the measurement of the mechanical properties is of chief importance in assisting him to determine the technical value of any metal or alloy and to select the most suitable alloy and treatment for any particular purpose. The tests made are either static, impact, or endurance tests, and technological tests.

Static Tests. *The Test Specimens.*—The test specimen must be chosen with regard to (1) the engineering standards for test specimens, and (2) the location of the test specimen so that the material of the test specimen will be representative of the piece as a whole, or of any particular part, whose properties are to be measured. If this cannot be accomplished by the use of one test specimen, a sufficient number should be taken to secure reliable results.

The importance with which the taking of the test specimen is regarded can be summed up in the words of Wawrziniok of the Royal Technical School, Dresden:

"Taking the sample (test specimen) correctly may be called the most important factor in the testing of materials. The most carefully performed experiment can be illusory if performed on a test specimen taken from an improper place, or under such circumstances that it is questionable if it is still identical with the material which is to be tested."

The recent advances in metallography have shown how decided can be the variation in structure and composition in one and the same piece, and this possibility must be taken into account if dependable results are desired. Beyond pointing out its importance, this subject will not be further considered here, as the problem of sampling iron and steel products has been very carefully and completely covered at another place.[1]

The size and shape of the test specimen are kept as nearly

[1] See BAUER and DEISS, "Sampling and Analysis of Iron and Steel." English translation by HAYWARD and HALL.

uniform as possible but they vary somewhat with the kind of a test to be made and the material to be tested. The dimensions of the test specimens have, for the most part, been agreed upon by the technical societies and are followed, if possible, even in scientific investigations.

The static tests usually conducted are tensile, compressive, transverse bending, shear and torsion tests. For a complete discussion of these tests, reference should be made to standard texts on the testing of materials, but at this place we shall limit ourselves to the tensile test.

The standard tensile test specimen which is used in the United States and England, is shown in Fig. 91. The diameter is either
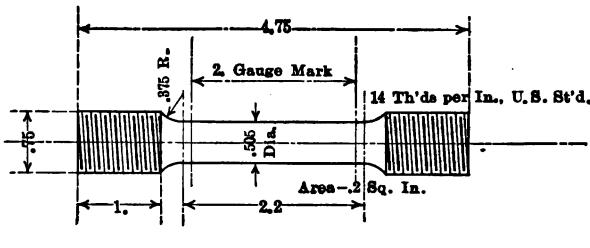
TENSION SPECIMEN STEEL
Dimensions in inches
FIG. 91.

0.500 in. or 0.505 in. If the latter diameter is used, the area of the cross section is 0.2 square inch and loads in pounds per square inch can be obtained by multiplying the actual load by the factor 5. The tensile test is made by applying an axial load[1] to the bar, measuring the load at all times as it increases up to the breaking

[1] That is, the assumption is made that the force is distributed uniformly over the cross section of the test specimen. This condition is approximated very closely in most of the standard European testing machines by supporting the test specimen, both above and below, by spherical bearing surfaces which are well oiled. Rigid jaws and threaded holders very frequently introduce bending strains to such an extent that the results of the test are thrown into doubt. Moore and Seely have recently shown that the elastic limit and yield point may be low by as much as 3000 to 7000 lb. per sq. in., if the test bar is pulled in wedge grips which are out of alignment (*Trans. Amer. Soc. Test. Materials*, 1916, Vol. 16, No. 2, p. 429). To overcome this defect in work in the Department of Metallography a pair of test bar holders was designed by Mr. Moody (student in metallography) and the writer to eliminate bending stresses. These were constructed by the Department of Experimental Engineering of the University (Minnesota), and are used when testing bars prepared in the metallographic laboratory.

point, and measuring the deformation which is produced in the bar. Deformations are measured on a standard length of two inches, called the "gage length," which is marked off along the length of the bar.

Plates, sheets, and other flat materials are tested by means of rectangular test specimens, but as there is little or no difference in the test, this point will not be considered here.

The "load" is measured in pounds per square inch by dividing the actual load on the test bar by the (average) original cross section; the "elongation" is measured by dividing the extension of the gage length by the original gage length, and expressing the result in per cent. The first applications of the load produce what are known as "elastic" deformations; *i e.*, such that if the load were to be removed, the bar would revert to its original length, as determined by accurate extensometer measurements. The maximum load, expressed in pounds per square inch or similar unit, which can be applied under conditions of elastic deformation, is called the "elastic limit" of the material. This load is not easily, and is therefore seldom, determined in practice, but many times it is taken as the first load to produce a permanent deformation of 0.001 per cent.[1] Furthermore, the deformation is in direct proportion to the force applied, as is required by Hooke's law. The maximum load to follow Hooke's law, assuming that deformations are measured accurately with an extensometer (at least to 0.0001 inch for a two inch gage length), is called the "proportional limit." This limit either coincides with or comes a little above the elastic limit. If the loading is continued still further, another phenomenon occurs which is common to iron and mild steel; *i.e.*, the bar suddenly elongates with no increase in the load. This is called "yielding" and the load at which it occurs, expressed in pounds per square inch, is called the "yield point."

Many metals and alloys break either at the yield point or even at a somewhat lower load. These materials, which can be deformed by only a small amount, are said to be "brittle." Other materials, belonging to the "ductile" class, can be deformed still further, but the deformations are all out of proportion to the loads applied. Such deformations above the elastic limit are

[1] At Grosslichterfelde the practice is to call the elastic limit the first load to produce a permanent set of 0.03 per cent., using an extensometer measuring to 0.00001 cm. on a length of 15 cm.

called "plastic" deformations and, if the load is released, the bar recovers only by an amount which is probably equal to the elastic deformation.   In other words, plastic deformation produces an appreciable "set" or "permanent deformation."   On increasing the load, there comes a time when the maximum load which the bar can sustain is reached.   This load calculated in pounds per square inch (using the original area) is known as the "tensile strength" of the material.   The bar does not necessarily break at this point, but further deformation, should it occur, is confined to a small portion of the length, known as the
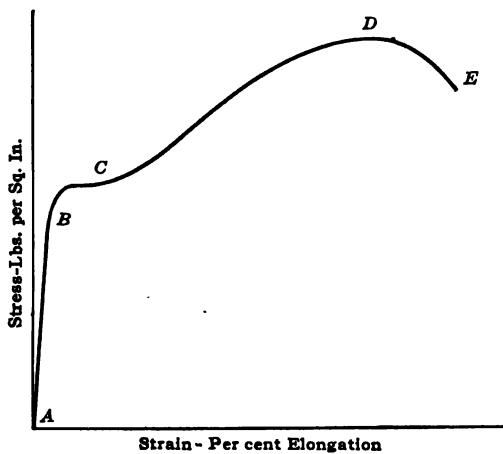
Fig. 92.—Stress-strain diagram.

"neck," and the load continually decreases until the bar finally breaks.   On account of the local deformation or necking, there is a very considerable reduction of area.

The course of a tensile test can be followed by plotting the stress, in pounds per square inch, against the strain, as elongation in per cent.   Such a "stress-strain" diagram for mild steel is shown in Fig. 92.   As long as the deformations obey Hooke's law, the line runs straight, as from A to B.   The point B is the limit of proportionality, while the elastic limit is made evident in no way by the stress-strain diagram.   The yield point is represented on the diagram by a nearly horizontal line, somewhat as at C. The deformations above the yield point are given by the line C–D–E.   The load at D is the maximum load, called the tensile strength, and that at E is the breaking load.   Deformations from

D to *E* are localized at the "neck." This diagram may also be obtained with an autographic or photograhic recording device on the testing machine which traces the curve as the test is made.

The points which are of general interest in the tensile tests are the strength and ductility of the material and the amount of work which is done up to the point of rupture.[1] The useful strength is the maximum stress which can be safely supported by the material, that is, the elastic limit. This is axiomatic for, by definition, any load above the elastic limit produces a permanent deformation, which engineering design seeks to avoid. Where the difficulty comes, is in measuring the elastic limit and it may be stated that this load, as such, is seldom determined. In practice either the proportional limit or the yield point is measured and, with this information, the part is so designed that in normal service the deformation will always be elastic.

Inasmuch as there still exists considerable confusion regarding the terms, or at least the usage of the terms "elastic limit," "proportional limit" and "yield point," a few words on the subject may be advisable. The ideas given out in the above discussion are admittedly correct and furthermore permit of direct experimental demonstration, although the commercial practice is to measure the yield point by the "drop of the beam," to call it the elastic limit, or the "commercial elastic limit" and to disregard the proportional limit altogether. While there is no justification for this procedure it could be overlooked as being "the practice" if all three points fell close enough together so that no serious errors were introduced, but many times the yield point lies considerably higher than the elastic limit. Moore and Seely[2] have shown that the ratio is at times from 110 per cent. to 112 per cent. while Lynch[3] has shown that it may be as high as 150 per cent. or even 190 per cent. Mitinsky, in an interesting discussion of the proportional limit, cited a case in which the proportional limit was as low as 25 per cent. of the yield point.[4]

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[1] The modulus of elasticity, or its reciprocal the specific elongation, is very important in engineering calculations, but, inasmuch as it is well known for the common materials, it is determined much less frequently. It is practically constant, and equal to 30,000,000 pounds per square inch for iron and the different steels, and is independent of heat treatment and other effects.

[2] *Trans.* Amer. Soc. Test. Materials, 1916, Vol. 16, No. 2, p. 426.

[3] *Ibid.*, p. 413.

[4] *Trans.* Amer. Inst. Min. Eng., 1916, Vol. 53, p. 161.

The material in question was rail steel which had received improper treatment in the rolling mill. Dr. A. Martens, late Director of the Royal Testing Laboratories at Grosslichterfelde, says in his book (1898), "This is indeed a serious matter; for this carelessness in diction may easily lead to a change of opinion of the qualities of the material by transposition of these limits, and actual injury may sometimes be done." (See English Translation, p. 30.)

Obviously the most logical procedure to secure the useful strength of a material, speaking particularly of steel, is to measure the proportional limit. The determinations should be made with an extensometer which, with the standard bar, will give the load at least to the nearest 500 lb. Many non-ferrous metals and alloys do not have a well defined proportional limit or yield point, and, to meet this case, Johnson[1] has suggested that the load at which the rate of deformation is 50 per cent. greater than at the start be taken as the "apparent elastic limit."

Under ordinary working conditions the material is not stressed above the elastic limit; but to guard against sudden fracture, should this limit be overstepped, material to be used for construction purposes should be able to deform appreciably before its breaking load is reached. Other materials, such as wire and pressed articles, must be deformed considerably while being worked into shape. This is the property of ductility or the ability to be deformed plastically, and, in the tensile test, it is measured by the total elongation and reduction of area. Materials which combine high ductility and great resistance to rupture with a high elastic limit are very desirable in engineering practice. This has lead to the determination of the elongation and reduction of area as quality factors by which, in combination with the elastic limit and tensile strength, to judge the material.[2]

An idea of the ductility may also be obtained from the difference between the yield point and the tensile strength. If the two limits fall together, or nearly so, the deformation is almost entirely elastic and as soon as plastic deformation commences, the material ruptures. Such a material is brittle. On the other hand, if the two limits are wide apart the material can usually undergo an appreciable amount of plastic deformation, and is

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[1] "Materials of Construction."

[2] The relationship between ductility and constitution of alloys has been dealt with by GUILLET, *Comptes Rendus*, 1907, Vol. 144, p. 1273.

said to be ductile. This rule is not at all infallible and the elongation proper should be relied upon to give the ductility.

Another property which enters in the judgment of materials for construction purposes, is toughness, although this is a property which can neither be readily defined nor measured. A definition of "static toughness" has been given as follows: Those materials may be classed as tough which offer considerable resistance to permanent deformation but which, once this resistance has been overcome, can be deformed plastically, but only by the expenditure of considerable energy. The resistance which must be overcome is proportional to the specific work of rupture and is represented on the stress-strain diagram by the area between the curve and the axis of stresses. The stress-strain diagram is seldom plotted so that formulæ have been advanced for the calculation of relative values of the toughness. In this way the area of the rectangle, tensile strength times elongation, gives an approximation of the static toughness. The following table is taken from the work of Heyn and is intended to show the value of such figures.

TABLE 10.—TOUGHNESS OF STEEL VS. CARBON CONTENT

Carbon, per cent.	T. S. atmospheres	Elong. $L = 11.3\sqrt{f}$	Average work = kgcm./cm.³
0.1	3,500	28.5	1,000
0.2	4,000	27.0	1,080
0.4	5,300	22.0	1,166
0.5	6,200	18.5	1,150
0.6	7,000	14.5	1,015
0.8	9,000	8.0	720
1.0	10,000	4.0	400

L = gage length.
f = cross sectional area.

Heyn remarks that the table shows that steels containing much over 0.4 per cent. C should not be used for construction purposes. The table also shows that the toughest steels contain several tenths of a per cent. of carbon. Even the area of the stress-strain diagram gives only static toughness and it is necessary to use impact tests to get accurate (relative) values of the toughness of materials which are subject to shock.

The Form of the Test Specimen.—To insure comparable results when using test specimens of varying sizes, two conditions

must be fulfilled. The strain distribution must be strictly similar in the test pieces, which (for the same material) will be so, according to Kick's law of proportional resistances, if the test bars are geometrically similar. There must also be sufficient material between the head of the test bar and the gage length, and the bar must be so shaped that there is no abrupt change in cross section near the gage length. This is to eliminate the effect of the frictional resistances which oppose contraction and the normal flowage of the material. The gage length in English and American standard practice is made four times the diameter of the test bar. In the Continental test bar this ratio is ten. On this account, elongations are apparently higher when measured with the standard American bar, principally because the excessive local elongation at the neck is distributed over a relatively shorter length. This affects the determinations of both the ductility and the toughness of ductile materials so that a statement of the elongation should always include a description of the test bar with which the determination was made.

A test selected from work done by the Midvale Steel Company illustrates the case. Two test bars from a one-inch round bar, with different gage lengths, gave the following results:

	T. S.	Y. P.	Elong., per cent.	R. A., per cent.
	Lb. per sq. in.			
5-in. gage length, ½-in. diam......	95,800	69,800	20.8	56.7
2-in. gage length, ½-in. diam......	96,500	65,000	28.0	57.6

The distribution of the elongation over a five-inch gage length obtained in the same laboratory is given in Fig. 93. It will be noted that the reduction of area is not affected by the gage length and hence should serve as a more reliable index of the ductility.

In ductile material, the flow of metal before rupture extends over the entire length of the parallel portion of the test specimen, assuming that the force applied is uniformly distributed over the cross section. Any influence which introduces secondary strains of a nature to hinder the elongation or contraction, will produce an increase in the tensile strength. Reduction of the ratio of the length of the strained portion of the bar to the cross

section, and excess material along the gage length, are generally responsible for secondary strains of this character. The tensile strength is not materially affected as long as the distance between shoulders remains greater than twice the diameter. Further shortening leads to a marked increase in the tensile strength and decrease in the ductility, as in one instance the tensile strength was increased from 88,000 pounds to 132,000 pounds and the reduction of area was decreased from 54 per cent. to 11 per cent. If the gage length is reduced to zero, the elongation and reduction of area very nearly vanish. A sudden change in cross section along the gage length interferes with the flow of material and likewise causes an increase in tensile strength and decrease of elongation and reduction of area.
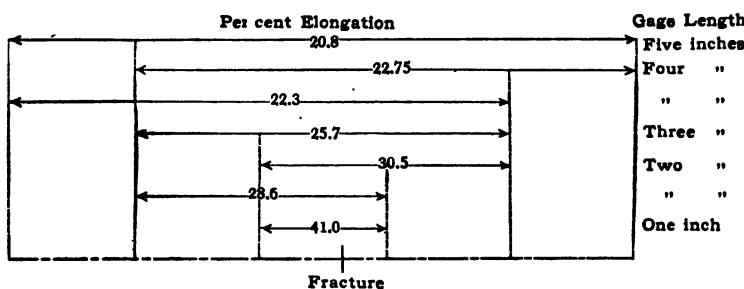
FIG. 93.—Distribution of the elongation over a five-inch gage length.

The Effect of the Rate of Applying the Load.—Wawrziniok[1] points out, in this connection, that the deformation of every substancce caused by a certain definite load, requires a certain amount of time for its completion. If the time allowed is insufficient, secondary strains, due to internal friction, arise which artificially raise the load required to produce the deformation. The additional force is regarded as an acceleration and therefore it increases as the time decreases, or as the rate of loading increases. It was pointed out by Wawrziniok that this effect is eliminated by using a speed corresponding to a 1 per cent. to 2 per cent. increase in elongation per minute, which, for a two-inch gage length would be 0.02 inch to 0.04 inch per minute.

It was recently shown by a committee of the American Society for the Testing of Materials that a variation in the speed of

[1] "Handbuch des Materialprüfungswesen," p. 34.

testing, at least over the range common in commercial practice, from one to six inches per minute, had no appreciable effect on the properties! Such a statement is really beside the point and the following practice has since been recommended by the Society regarding the speed of testing:

TABLE 11.—A.S.T.M. STANDARD RATE OF LOADING—TENSILE TEST

Sepcified minimum tensile strength, lb. per sq. in.	Gage length, inches	Maximum crosshead speed	
		Yield point	Tensile strength
		Inches per minute	
80,000 or under.................	2	0.50	2.0
	8	2.00	6.0
Over 80,000.....................	2	0.25	1.0
	8	0.50	2.0

A speed of 0.125 inch per minute, as a maximum, is recommended for determining the commercial elastic limit of forgings and cold-rolled axles. This speed is lowered to 0.025 inch per inch of gage length, in determining the limit of proportionality.

Campbell[1] gives values of the tensile properties for speeds ranging from 0.1 inch per minute to 4.5 inches per minute on structural steel. The yield point is shown to increase from 39,-000 to 46,000 lbs., and the tensile strength from 59,000 to 62,000 lbs.

The exact influence of the rate of loading necessarily varies with the material and is more pronounced in the case of copper, zinc, aluminum, and tin, than it is in the case of iron and steel. For, example, Capp has found that the real elastic limit of manganese bronze is much lower than that which is usually found in rapid testing, the amount being as much as 40 to 50 per cent.[2]

The behavior of metals in other static tests, although of great technical importance, will not be considered in detail here. Standard books on the testing of materials should be consulted.

Impact Tests for Toughness.—The writer has attempted else-where[3] to point out the necessity of using other tests for the

[1] "Structural Steel," p. 253.

[2] "Castings," 1910, Vol. 5, p. 201.

[3] *Bull.* Amer. Inst. Min. Eng., February, 1919; *Journ.* Amer. Steel Treaters' Soc., May, 1919.

materials used in construction. This necessity arises from the fact that materials, in service, very frequently behave as if brittle, although they possess the requisite degree of ductility as measured by the elongation and reduction of area in the tensile test. Brittleness, according to Le Chatelier, may be due to two different causes.[1] The first cause is to be found in the nature of the metal. Brittleness which is due to this cause can be traced to (1) the chemical composition, (2) the chemical constitution, (3) the structure, more in particular as affected by heat and mechanical treatment, (4) to cold work, (5) to heterogeneity, slag enclosures, segregation, etc. These separate causes will be discussed under Technical Metallography, but it is well to bear in mind, for the present, the different points in connection with the metal itself which can give rise to undue brittleness.

The second cause of brittleness is found in the external conditions affecting the metal. These causes may be subdivided into (1) the rate of applying the load, (2) the temperature, (3) the form of the piece, and (4) diverse causes such as excessive vibrations in conjunction with a steady load, etc.

One of the outgrowths of this more or less abnormal behavior is the so-called "drop test," commonly used in this country in testing railway material. Steel rails are tested by allowing a heavy weight to fall on a short length (discard) which is held on two supports one yard apart. The impact either fractures the rail or bends it through a certain angle. If the test rail is capable of sustaining the required impact without deforming to too great an extent, the rails represented are passed as being satisfactory. In this way certain of the brittle rails are detected and prevented from entering the service; and there can be little doubt that rails failing to pass the drop test should be rejected. The weak point of the test is that certain rails, which should be rejected, are entirely missed by this test and are passed into service. This is principally because defective portions of the rail, sufficient to cause the ultimate failure of the rail in service, are supported by the sound portions during the brief interval of the test, and the rail as a whole appears to be uniformly sound. This deficiency of the drop test should undoubtedly be remedied by makng a macroscopic examination of the cross section for segregation, pipe, or other defect. Furthermore, the ability of the material to stand one heavy impact offers no positive assur-

[1] "Contrib. a l'étude de la Fragilité dans les Fers et les Aciers."

ance that lighter stresses, sufficient to produce plastic deformation in some portion, or portions, of the rail, if often enough repeated, will not cause ultimate failure.[1]

The drop test, properly viewed, is a transverse bending test in which the rate of applying the load is comparatively rapid. As a simple means of carrying out a transverse test, the drop test has much to commend it, but there seems to be no reason to expect an impact to develop undue brittleness in a rail which a simple tensile would miss. This is because, as we have already seen, increasing the rate of loading has merely a quantitative effect. but qualitatively the properties remain the same. That this is so, is shown by an abundance of evidence[2] including even that of the drop test itself.

Even so, there remain those cases in which materials fail as if due to lack of toughness even though the tensile test shows them to be ductile. It has been the writer's experience that these failures are many times due to the shape of the part, or rather to a decidedly non-uniform distribution of the strains, or else to the presence of internal flaws due to foreign inclusions, segregations, and the like. The effect is to produce brittleness, especially where the stresses are repeated a large number of times as has been recognized for some time now, particularly in France and Germany. The result is that we now have the impact test on notched bars, as a supplement of the usual test, its particular virtue being that it develops brittleness (or toughness) in a

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[1] The inability of the drop test to discriminate between sound rails and segregated rails is shown by the work of BURGESS and HADFIELD, *Trans.* Amer. Inst. Min. Eng., 1916, Vol. 51, p. 862, and *Journ.* Iron and Steel Inst., 1915, No. 1, Vol. 91, p. 40. Its inability to discriminate between rails which have been finished hot and rails finished 500°F. lower, is shown by the work of SHIMER, *Trans.* Amer. Inst. Min. Eng., 1916, Vol. 51, p. 828.

[2] CONSIDERE, "Contrib. a l'étude de la Fragilité dans les Fers et les Aciers," p. 3.

PLANK, *Zeit.* ver. deut. Ing., 1912, Vol. 56, pp. 17 and 46.

DE FREMINVILLE, "Contrib. a l'étude de da Fragilité dans les Fers et les Aciers," p. 475.

See also PIERRE BREUIL, *Journ.* Iron & Steel Inst., 1904, No. 1, p. 413; HATT, *Proc.* Amer. Soc. Testing Materials, 1904, Vol. 4, p. 282.

FREMONT, "Contrib. l'étude de Fragilité dans les Fers," p. 150; CHARPY, *ibid*, p. 213.

MARTENS, "Handbook of Testing Materials," p. 233.

See also the discussion by CHARPY of the paper by the author, *Bull.* Amer. Inst. Min. Eng., April, 1919.

manner which, in many important cases, is entirely missed by the tensile test for ductility.

The Notched Bar Impact Test.—In automobile or machine design, as well as in many other places, parts are so designed that a sudden or rapid change in cross section, here referred to as a "notch," is many times unavoidable. Under such circumstances the behavior of the material is much different than it would be if the section were uniform and the strains were uniformly distributed. Examples of such conditions are very numerous and only a few need be given here, such as right-angled shoulders cut on axles or shafts, the entrance of the piston rod into the piston, rivet and bolt holes, and so on. Defects in drop forgings due to improperly made dies, rough tool marks, careless machining and other defects not due to design, are equally dangerous.

It has been customary in the past to test materials by the various static and dynamic tests enumerated above and, from them, to judge whether the quality of the material is sufficiently high to warrant its use, regardless of the design of the part or its relationship to other parts or of possible defects due to faulty workmanship. In the above cases the usual tests are unable to differentiate clearly between materials which will probably stand up and those which are very likely to fail. Furthermore the tensile test does not bring out, adequately, the value of heat treatment as applied to steel nor the full value of adding special elements to steel.

It may be well to bring out, by a few simple examples, the effect of a notch on the properties, a notch being a rapid or sudden change in cross section which greatly localizes the strains at the diminished section. The effect of a notch on the properties of metals is well illustrated every time a blacksmith nicks a.bar to break it off at any particular point. Even a blow by the hand produces strains at the base of the notch well in excess of the resistance of the material and hence produces the fracture. A similar blow on an unnotched bar would merely bend the bar over. Thus it is that a bar, even though made of normally tough material, if notched, may behave as if brittle. Koenigsberger[1] has shown by means of glass models that notches localize the strains and that the neutral axis of a stressed bar runs close to the peak of the notch, instead of remaining in the middle sec-

[1] *Proc.* 4th Congress Intern. Assoc. for Testing Materials, Brussels, 1906, *Paper* C4d.

tion. Heyn[1] has shown that a lead bar cut with a notch has an entirely different strain distribution under bending from that of a similar bar without a notch. The volumes of the strained parts were as 1 : 3.76 and the maximum fiber elongations, measured by the distortion of 5 mm. squares, were 120 per cent. and 70 per cent., for the notched and unnotched bars respectively. But to get a correct idea of the maximum deformation, the extension of the width of a line at the apex of the notch was determined. The original width of the line was 0.25 mm. but after deformation it was found to be 5 mm., which gave a deformation of 1700 per cent. It has also been shown by Leon,[2] that a transverse notch cut in a tensile test bar produces an uneven distribution of strains over the cross section at the base of the notch, the greatest strains coming at the apex of the notch. These cases illustrate the "notch effect" as it occurs in ordinary metals, which is to localize the strains in the neighborhood of the apex of the notch, at times to such an extent that they may be far in excess of the resistance of the material under tension. In excessively brittle materials, the multiplication of the maximum fiber stress is even more excessive. An example of a notch in such materials, is the small file scratch made on a glass rod to assist in breaking off any particular length.

It is likewise known that the severity of the notch effect increases as the angle of the notch decreases. On this account the notch effect increases in most materials when fracture starts, because the angle of the fracture is generally less than the angle of the original notch. Certain pliable materials, or those that are "self healing," of which lead is an example, behave in the opposite manner, since the notch becomes more rounded with distortion. In the same way a material of high notch toughness is much less dangerously affected by a notch than one with low notch toughness, a point that will receive consideration further on.

In recognition of the prevalence of the notch effect in engineering practice[3] and of the peculiar brittleness which is caused thereby, the so-called notched-bar impact test has been devised.

[1] MARTENS-HEYN, "Handbuch der Materialienkunde," IIA, 374. Berlin, 1912.

[2] "Oester. Wochenschrift f. d. oeffentlichen Baudienst" (1908) 29, 43.

[3] The writer has pointed out a number of typical examples of the notch effect, as it sometimes occurs, in the papers referred to and the value of heat treatment, in this connection, is particularly emphasized.

In its present form, the test is the result of systematic experiments of two decades or more by Barba, Fremont, Charpy, Ast and others,[1] which culminated in the reports of Charpy to the International Association for Testing Materials and of Ehrensberger to the German Society for Testing Materials.[2] The accumulation of evidence over this period made possible the establishment of a standard test, so that now it can be safely stated that the notched-bar test is capable of supplying the information relative to the notch toughness which the tensile test gives in but an imperfect, and often directly misleading manner. That is, the impact test on notched bars is better able to develop the single property of toughness, and to that extent it is more discriminating than the static tests. This test has shown further, it should be pointed out, the great danger of angular notches or sudden changes in cross section, segregations and foreign inclusions or "internal notches."

In these tests it is essential to use test specimens, wherever possible, of identical size and shape. The test bars now used are either 10 × 10 × 53.3 mm. or, as they are sometimes made, 10 × 10 × 60 mm. for the small bar and 30 × 30 × 160 mm. for the large bar. Charpy has recently recommended the deep notch, which for the small bar is 3 mm. in diameter and 5 mm. deep. This notch is made with a drill bit, tangent to the center line of the specimen, and cut through to the surface with a hack saw. The advantages of this notch are said to be: (1) It can be determined with great exactness, since it can be obtained with the drill; (2) Like all deep notches, it reduces the total work of rupture and the proportion of the work of bending in reference to the work of detaching the surfaces, this latter being the most interesting phenomenon of fragility; (3) Its making does not affect the physical state of the metal around it. The testing machines designed by Charpy to deliver impacts of either 10, 75, or 250 meterkilograms have been accepted as standard, so the test is frequently referred to as the "Charpy test." Further, it is desirable always to use the same testing machine to secure the greatest uniformity.[3]

[1] See *Proc.* Intern. Assoc. Test. Mat., 1901, 1906 and 1909.

[2] *Stahl u. Eisen*, 1907, Vol. 27, p. 1797.

[3] It has been shown recently that comparable results are obtained, even if different types of testing machines are used, so that this condition need not always be strictly observed.

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The resistance to impact is determined from the weight of the pendulum and the height of fall necessary to fracture the test bar (taken as the height of fall minus the height of recovery) and is calculated as meterkilograms per square centimeter cross sectional area at the apex of the notch. This impact figure is taken as a measure of the "notch toughness," by which is meant the ability with which a material can resist an impact when in a notched condition and transform the energy of the impact into work of deformation. The temperature of the test should be recorded as there is an appreciable variation in notch toughness with temperature.[1]

It would hardly be feasible to enter into a more detailed discussion of the impact notch test here[2] but at least a few examples can be cited to bring out the important points.

Ehrensberger incorporated into his report to the German Society the results of numerous tests showing the relative behavior of certain steels in the ordinary static test and in the notch test, from which the following are taken.

TABLE 12.—COMPARISON OF THE TENSILE TEST WITH THE CHARPY TEST

Carbon Steels (Forged)

No.	T. S., lb. per sq. in.	Y. P., lb. per sq. in.	Elong., per cent.	R. A., per cent.	N. T., mkg. per sq. cm.	Remarks
1	61,500	32,700	26.5	64	4.6	Forged hot.
2	64,100	36,100	26.0	70	20.4	Correctly forged.
9	71,600	42,000	24.5	70	22.6	
10	71,800	40,000	26.4	60	4.7	Railway axle.
25	142,200	93,000	12.1	36	8.5	High carbon.

[1] Ehrensberger gives the following figures for steel:

Temperature	Notch toughness, kgm. per sq. cm.
− 20°C.	4.24
− 1°C.	16.29
+ 20°C.	24.69
200°C.	33.90

[2] See HEYN, "Materialienkunde," IIA, p. 392.

Nickel and Chrome-nickel Steels

51	72,800	58,200	23.3	70	42.1	
69	130,000	108,600	15.1	62	22.1	
71	142,200	118,200	13.3	56	19.3	
75	270,200	232,500	6.5	31	8.3	

Cast Steel, Untreated

161	68,000	37,700	22.9	51	3.7	

[1] Elongations are for a gage length equal to ten times the diameter.

Comparing numbers 1 and 2, we find from the notch test that No. 1 is of inferior quality, due to forging too hot; this was not indicated by the static test. Numbers 1 and 25 show that a mild steel improperly treated, may be less safe in service than a higher carbon steel properly treated, although the static test shows No. 1 to be more ductile. No. 10 is from a railway axle which broke in service without apparent cause. The impact test developed comparative brittleness which was in no way indicated by the static test. A comparison of the carbon steels with the nickel and chrome-nickel steels shows that the higher quality of the latter, especially the toughness, is expressed more clearly by the impact test. Numbers 69 and 71 of the special steels have about the same notch toughness as numbers 9 and 2 of the carbon steels, and yet 69 and 71 are considerably stronger than 9 and 2. Comparing test numbers 2 and 51, which, from the tensile tests, would be expected to show greater toughness for the carbon steel, we see that the special steel is in reality considerably tougher. No. 161 shows that cast steel may have an elongation and reduction of area comparing favorably with forged steel, at times even greater, but it can hardly be assumed, even on those grounds, that castings are the equal of forgings. The impact test reveals the true character of cast steel.

Charpy included in his official report to the Copenhagen Congress various examples to illustrate the practical applicability of the impact test. The life of the piston rod of a steam hammer was increased from three months, when made of mild steel, to over six years, by selecting heat treated steel which possessed high notch toughness. He also considered the application of the notch test to the testing of armor plate and showed it to be of great value.

In Charpy's report of 1909, an interesting case was cited to show that the notched-bar test can give information regarding steel that is in no wise suggested by the tensile tests, either static or dynamic. The results obtained with two steels *A* and *B*, really the same steel in two different conditions of heat treatment, are given in Table 13. Not even the resistance to fracture produced by a weight falling from a height of about 100 ft. (30 m.) as given in the next to the last column, indicates the excessive brittleness of steel *B*. The microstructure at once showed that *B* is in a much poorer condition than *A*.

TABLE 13.—RESULTS OBTAINED BY NOTCHED-BAR TESTS

Steel	E. L.	T. S.	Elong., per cent.	R. A., per cent.	Static resist., mkg.	Tensile impact resist., mkg.	Charpy test, mkg.
	Lbs. per sq. in.						
A	42,800	59,900	32.0	67.2	179.5	205	44.0
B	42,700	62,700	32.0	65.6	185.0	195	2.7

The design of many machine parts, which are subjected to sudden and vibratory stresses, is such that sudden changes in cross section are unavoidable and at times purposely introduced. In these cases, the notch test is particularly desirable to assist in selecting the proper material, as it shows directly the ability of the material to resist the notch effect.

Various objections have been raised to the adoption of the notched-bar test, one of the principal ones being the so-called lack of uniformity of the results. This question has been gone into rather thoroughly by Prof. Howe,[1] and more recently by Charpy and Cornu-Thénard.[2] In a number of cases the results of the notched-bar impact tests are not as concordant as might be desired. It is the opinion of many experimenters, however, that variations in the impact resistance of supposedly similar test bars are due to actual variations in the material, the wide scale of the Charpy test throwing them into greater prominence than do the usual tests. The truth of this contention is demonstrated by the recent work of Charpy and Cornu-Thénard, who, by using exceptionally uniform and homogeneous bars, secured check results as close as 1 to 2 per cent. and scarcely ever varying

[1] *Trans.* Amer. Inst. Min. Eng., 1913, Vol. 47, p. 501.
[2] G. CHARPY and A. CORNU-THÉNARD, *Rev. de Mét.*, 1917, Vol. 14, p. 84; *Journ.* Iron & Steel Inst., 1917, No. 2, p. 61.

as much as 4 per cent.[1] The results obtained by the com-
mission of the German society were sufficiently concordant
to lead to the adoption of the test and the minor variations were
not permitted to mask the fact that the notched-bar test is capable
of yielding valuable information that the tensile test does not..

The writer is informed that at least one steel plant, which
has done considerable work on the notched-bar test, including
the Charpy test, has found the concordance of results to be
very satisfactory and capable of yielding possible differences of
impact resistance of the order of magnitude of 1 : 20.   Thus, it
would seem that lack of concordance can now no longer be ad-
vanced as an objection to the adoption of the Charpy test.

There has also been considerable objection to the presence
of the notch in the test bar, the idea being that the nick localizes
the breaking point and so does not test the weakest cross
section.[2]   This is undoubtedly a point that must be considered
when using the Charpy test.   For example, if there is excessive
segregation, it is quite possible that the base of the notch will
come at the weaker part and so lead to low results.   At the
same time such a variation in results is a valuable indication of
segregation, so that by breaking a number of test bars not only
can the average value be obtained but non-homogeneity in the
material itself can be determined.   The object of the Charpy
test is not so much to test any particular test bar,[3] as it is to
test the relative toughness of a certain material[4] or the efficacy of
a certain heat treatment.   Moreover, it is quite customary,
at least in certain quarters, to precede the Charpy test by

[1] Even a 4 per cent. variation could scarcely be objected to on the score
of lack of concordance in the light of the present practice in pulling test bars.
A 4 per cent. variation would mean a variation from 49,000 to 51,000 lb.
per sq. in., a variation that is much less than variations due to improper
rate of loading, improperly holding the test bar in the machine, and in par-
ticular to the general neglect of the proportional limit in favor of the yield
point as a measure of the elastic limit.

[2] H. M. Howe, "The Resilience Test," *Met. & Chem. Eng.*, 1917, Vol. 17,
p. 298; Walter Rosenhain, "Introduction to the Study of Physical
Metallurgy," p. 237, 1915.

[3] The use of the Charpy test as an acceptance test would hardly merit
discussion until the value and importance of the test proper is generally
conceded.   See Klein, *Stahl u. Eisen*, 1914, Vol. 34, p. 136.

[4] This statement is subject to the reservation advanced by Prof. Howe
that, due to the greater plasticity of low-carbon steels, we cannot directly
compare steels of essentially different carbon contents.

macroscopic tests for gross segregations in order that variations due to such segregations may be eliminated.

Recently there has been an attempt to eliminate the notch from impact testing, in the impact shear test described by Dr. McAdam.[1] In this test, an unnotched bar is sheared by an impact while the impact figure is read the same as in the Charpy test. It has been argued[2] that by eliminating all except one stress, the impact shear test is superior to the Charpy test. There can be no doubt that materials to be subjected to shearing stresses by impact (in an unnotched conditon) might well be tested by this method; but, from the very nature of things, no test on unnotched bars can be substituted for a notched-bar test. The correctness of this assertion is supported by the results of the impact shear test itself, according to which such materials as properly heat-treated nickel and chrome-nickel steels fail to give as much resistance to impact as carbon steel or even ingot iron.

Summary.—Undoubtedly the notch effect is more prevalent in engineering practice than is generally realized, while it may also be stated that the ills accompanying this effect are very much underrated. Under these circumstances it is now no longer sufficient to test materials in a simple or unnotched condition. Such a simple material as a steel splice bar used in track construction, from the writer's observations, should be tested for notch toughness for, while it is possible, by design, to give sufficient mechanical strength, it is only by heat treatment that the requisite degree of resistance to the notch effect can be imparted to the bar. The logical test in such cases, and the only one capable of yielding reliable results, is the notched-bar test. This test should supplement the usual tensile or hardness tests and its results used as an index of the resistance of the material to the notch effect.

Vibratory Stresses.—Alternating or repeated stress tests (sometimes called fatigue tests) have been introduced on account of the fact that stresses which are below the tensile strength or even below the elastic limit, if repeated a sufficient number of times, will lead to the failure of the material; thus, railway axles and other machine parts similarly loaded have been known to break on this account. Consequently it is necessary to know the effect of repeated stresses of various magnitudes on the resistance of materials. This led Woehler in 1870 to make a system-

[1] *Trans.* Amer. Soc. Test. Mat., 1916, Vol. 16, No. 2, p. 292.
[2] Personal communication.

atic study of the vibratory strength of metals, which work was the first of its kind.[1] As a result of these investigations, two principles underlying the resistance of materials to repeated or alternating stresses were enunciated. The first principle of Woehler is made clear by reference to Fig. 94. The curve shows that as the maximum stress applied decreases, the number of applications of the load which the material can stand, increases, until the load becomes so small that there is little or no danger of rupture within the life of the piece. The correspond-
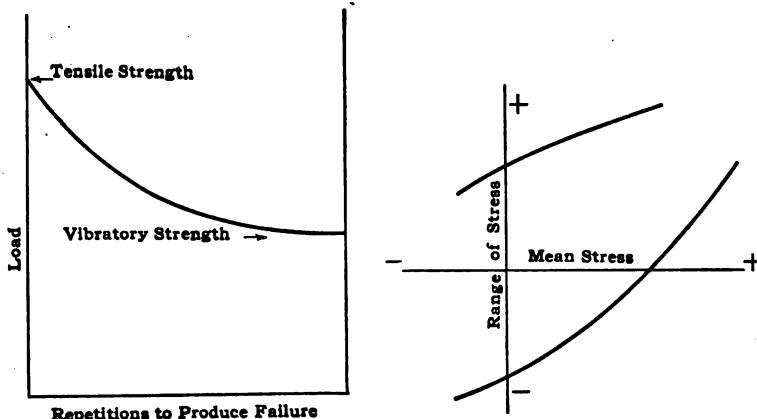
FIG. 94.—Woehler's first principle.

FIG. 95.—Woehler's second principle. Vertical distances between the curves give safe ranges of stress.

ing stress range is called the "maximum safe range of stress." This determination is purely empirical as it now seems clear that any load, if applied a sufficient number of times, will cause the failure to occur. On the curve in Fig. 94 the safe load is apparently the horizontal which the curve approaches asymptotically, but, as has been pointed out by Upton and others, the position of·the asymptote is purely a question of the scale used.

The second principle of Woehler is that safe loading depends on the range of stress applied and not on the maximum value of the stress, but that, as the maximum stress increases, the range of stress which can be safely endured, decreases. This principle is shown in Fig. 95. Values of the mean stress (that is, half the sum of the maximum and minimum stress) are plotted as abscis-

[1] For the work of WOEHLER, see *Zeit.* f. Bauwesen, Vols. 10, 13, 16 and 20; also *Engineering*, 1891, Vol. 11, p. 199.

sæ. The corresponding limiting values of the safe range of stress are given by the two lines which pass through values approximately equal to the elastic limits in tension and compression for a zero mean stress, and the yield point, for a mean stress equal to one-half the range of stress. This statement would not apply strictly for large values of the repetitions of stress but seems to hold very well for 1,000,000 repetitions, as is shown for the following table taken from the work of Smith.

TABLE 14.—RELATION BETWEEN STATIC AND ENDURANCE TESTS OF STEEL

Carbon, per cent.	Lt. pr.	Y. P.	Range ÷ 2, for zero mean stress		Range, for mean stress = range ÷ 2	
	Lb. per sq. in.		Woehler test	Smith test	Woehler test	Smith test
0.13	28,224	38,528	26,880	29,120	41,440	38,080
0.27	33,600	41,400	30,300	31,360	45,920	42,560
0.34	36,950	46,800	32,480	33,600	48,160	49,280
0.45	39,100	53,760	34,720	32,480	53,088	49,280
0.57	45,920	54,500	38,080	38,080	57,790	54,880

Woehler test-number of repetitions = 1,000,000.
Smith test-figures represent "yield ranges" determined by Smith's accelerated test.

It is the assumption in this table that the values of the elastic limit are the "true elastic limits;" *i.e.*, the value in case the limit in tension is equal to the limit in compression. If one of the limits is an "exalted" elastic limit due to overstrain the results may vary considerably from those given here.[1]

By way of illustrating the second principle, Woehler cites the case of iron, which he found could withstand vibrations, with equal security against rupture by tearing or crushing, within

[1] According to the work of Bauschinger, a stress above the elastic limit in tension causes an increase in the elastic limit in tension and a corresponding decrease in the elastic limit in compression and, vice versa, a stress above the elastic limit in compression causes a similar increase in the elastic limit in compression and decrease in the elastic limit in tension. On this account, the elastic limit, as ordinarily determined, may be a transitory elastic limit due to the previous history of the material. The elastic limit in tension may be made equal to the elastic limit in compression by stressing first slightly above the elastic limit in tension and then slightly above the elastic limit in compression. When the two elastic limits are equal to each other, the material is said to be in a "cyclic" state, and the corresponding elastic limit is called the "true elastic limit."

the following limits: between $+17,500$ pounds per square inch and $-17,500$ pounds per square inch; between $+33,000$ pounds per square inch and zero; and between 48,500 pounds per square inch and $+26,500$ pounds per square inch.

It has been noted that the maximum stress and the number of alternations when plotted on logarithmic paper fall on a straight line. An equation representing this relationship has been given in the form

$$S = KN^m$$

or

$$\log S = \log K + m \log N$$

where S is the maximum stress, N is the number of repetitions to cause failure, and K and m are constants.[1]

It has been pointed out by Moore and Seely that the exponential formula holds better for low values of N than for high values (above 10^6) and they have therefore suggested a modified formula which might better be used when calculating the allowable stresses of parts which must endure a large number of repeated stresses.

The alternating stress test has been used to determine the limiting values of the stresses to which any particular material can be safely subjected, if the number of alternations is to run up into the millions. Various experimenters have shown that such a limiting stress, provided the lower limit of the range is zero, runs parallel to, and in many cases is equal to, the yield point. Thus these tests have shown that the limiting value in the case of steel increases with the carbon content, or even with the phosphorus content, as both of these elements raise the elastic limit. This fact limits the commercial usefulness of the test for it is seldom that materials fail by simple fatigue in practice. About the only time failure is brought about by simple fatigue, that is, because the number of reversals exceed the permissible number for the range of stress, is in case the elastic limit has been unduly lowered as, for instance, by overannealing (Arnold).

If the stress varies from a tension to a compression so that the maximum tension is equal to one-half the range, the maximum

[1] See for example, papers by BARQUIN, *Proc.* Amer. Soc. Test. Mat., 1910, Vol. 10, p. 625; UPTON and LEWIS, *Amer. Mach.*, Oct. 17 and 24, 1912; MOORE and SEELY, *Proc.* Amer. Soc. Test. Mat., 1915, Vol. 15, Pt. 2, p. 438 and 1916, Vol. 16, Pt. 2, p. 470, which contain much valuable information on the subject of alternating stresses.

allowable stress may fall under the elastic limit, a point which has occasioned no little surprise and speculation. This has been brought out by a number of experimenters among whom may be mentioned Smith,[1] Howard,[2] and Boudouard.[3] In a discussion of this point, Le Chatelier pointed out that while it is true that materials are elastic, no material possesses perfect elasticity. In reality every deformation, no matter how small, produces two effects; as soon as the stress is relieved the material tends to return to its original form, which is the influence of elasticity; however the material does not assume its original dimensions as soon as the stress is relieved—the operation requires a certain length of time, which is the effect of viscosity. If the material is subjected to alternate tension and compression, it is forced to return to its original shape by overcoming the viscosity, whice necessitates a certain amount of work being done on the bar, which may be called the elastic hysteresis. Finally, a deformation always produces a very small, though finite, permanent deformation. The direct consequence of these permanent deformations is the gradual disruption of the crystalline structure, which manifests itself earlier (assuming a constant maximum) if the stress varies from a tension to a compression and may readily occur even though the maximum stress lies below the elastic limit.[4]

While these tests have developed many interesting points in connection with the properties of materials and their probable behavior in service under vibratory stresses, they are not practical tests to carry out. On the basis of the knowledge gained so far it is possible to use the limit of proportionality, and a factor of safety, to insure keeping the working stresses within the maximum safe range. At places, the use of the tensile strength in this connection has been advocated. Such practice must necessarily be in error, however, inasmuch as the elastic limit and the tensile strength are not parallel and a high tensile strength does not necessarily mean a high elastic limit, and it is loading above the elastic limit which must be particularly guarded against.

[1] *Journ.* Iron & Steel Inst., 1910, No. 2, p. 246.

[2] *Proc.* 5th Congress, Intern. Assoc. Testing Materials, Kopenhagen, 1909.

[3] *Proc.* 6th Congress, Intern. Assoc. Testing Materials, New York, 1912.

[4] The hysteretic effect of viscosity has been dealt with in particular by BAIRSTOW, *Phil. Trans.* Roy Soc., 1910, A, Vol. 210, p. 35; MOORE and SEELY, *Proc.* Amer. Soc. Test. Mat., 1915, Vol. 15, Pt. 2, p. 437; and by PROFESSOR SMITH.

These tests have been of paticular importance in one respect in that they have served to demonstrate the danger of abrupt changes in the cross section (notches), be they even so minute as a scratch. Woehler showed from tests on filleted and unfilleted test pieces taken from a railway axle, the much greater safe range possessed by the former. The following table for wrought iron and steel shows the effect of a notch on the maximum safe load.

	Reversals	Safe load	
		Rounded fillet, lb.	Square corner, lb.
Wrought iron....................	1,000,000	17,500	14,200
Steel...........................	14×10^6	44,500	29,150

Smith[1] cites a case in which the number of reversals decreased from 739,400, for a smooth bar, to 3000 for a bar with square shoulders, the range of stress being the same in both cases. The presence of under-cuts, due to careless machining, was shown to be equally as dangerous, as the number of reversals was reduced thereby to about 5 per cent. of the normal. The danger from this source is so great that even small transverse scratches, used to mark off the gage length, lead to premature failures. The careful machining and polishing required, as a consequence, seriously militate against the commercial use of this test. By the same token machine parts which are subject to fatigue should be made of uniform cross section and polished to eliminate scratches.[2]

Two important technical questions connected with the use of materials in engineering practice are as to the effect of rest and cold working on the resistance of steel to fatigue. It appears from the work of Moore and Putnam[3] that neither of these factors can be relied upon to effect any material improvement. On the other hand certain corroding agents may materially lower the resistance to fatigue, as has been shown in the case of brass.[4]

Various means have been devised to determine the relative vibratory strength and the limiting safe range of stress in a short space of time. Accelerated tests of the first kind have been de-

[1] *Loc. cit.*, p. 260.

[2] Even in the static tensile test, the rough machine marks should be removed by polishing.

[3] *Bull.* Amer. Inst. Min. Eng., February, 1919.

[4] HAIGH, *Journ.* Inst. Met., 1917, No. 2, p. 71.

scribed by Kommers[1] and Upton.[2]   In these tests the specimen is stressed above the yield point by bending backward and forward through certain definite angles.   The principal objection to this test, as has been pointed out by Rosenhain[3] is that two metals may be classed in one order, when the stresses applied are above the yield point, and classed in the opposite order if stressed below the elastic limit, so that the results may very well be illusory.

Professor Smith has described accelerated tests which are not open to the same objection.   In his tests, values of the limiting range or its equivalent, the "yield range," are determined for certain values of the mean stress.   The idea employed in the tests is that, after converting the material from its primitive state into its cyclic state, alternating stresses of known amount are applied to establish a certain "range of stress."   The corresponding mean stress, for which the range of stress in question is the "limiting range," can be determined by alternately applying mean stress in tension and in compression in gradually increasing amount and noting the maximum amount of mean stress which can be applied before yielding takes place, and making certain that the material yields for the same values of the mean stress in tension and compression.   By using a series of different limiting ranges, different values of the mean stress can be obtained without injuring the bar.   The data when plotted give curves similar to those in Fig. 95.   This method is based upon the assumption that the "yield ranges" correspond to the Woehler "limiting ranges" which are ordinarily secured only after long and tedious experimentation.   Values of the "yield range," as determined by Smith's test, are reproduced in Table 14 alongside the Woehler "limiting ranges" and seem to indicate that the Smith test is capable of yielding reliable results.

An impact fatigue test, the results of which agree very closely with practice, has been devised by Professor Arnold.[4]   In this test, the specimen, which is clamped in a vise, is bent backward and forward by means of a collar which fits loosely around the free end.   There is a certain amount of play between the striking edge of the collar and the test bar, so that a blow is delivered

[1] *Proc.* 6th Congress Intern. Assoc. Test. Mat., New York, 1912.
[2] *Sibley Journal of Engineering*, Cornell Univ., October, 1913.
[3] "Introduction to Physical Metallurgy," 1914, p. 231.
[4] *Proc.* Inst. Civil Eng., 1903, Vol. 154, Supplement.

at each reversal. The strains in the test bar are due partly to impact and partly to bending and are generally fairly high. During the test the bending moment is kept constant which has given rise to the objection that certain test bars will be stressed above the elastic limit while others will be stressed below the elastic limit so that no true basis for comparison is afforded. However, this test brings out at once the lesser toughness of the high carbon and high phosphorus steels, which is missed by the Woehler test.

The practical application of the data obtained from alternating stress tests has been considered by Moore and Seely (*loc. cit.*) whose work should be referred to for greater details. They have shown how formulas may be used to determine the maximum safe load for service conditions and have brought out the important point that at times the static conditions of loading and that, at other times, the endurance conditions, determine the conditions of safe loading.

The Influence of Temperature on the Tensile Properties.[1]— The average temperature at which tests are commonly carried out is 20°C. or room temperature, while materials are used at temperatures ranging from −30° (rails and bridge members) to 400°C. for boiler and furnace parts. That makes it necessary to test materials at temperatures above and below room temperature so that the parts can be so designed and constructed that they will not fail when used at those temperatures.

The value of such information was early recognized by A. Le Chatelier who determined the effect of temperatures up to 450°C. upon copper, aluminum, nickel, silver, aluminum bronze, a copper-iron-nickel alloy and zinc. This investigation brought out the effect of temperature in materially lowering the tensile strength, which, in the case of copper and aluminum was noticeable at 100°C.[2] Heyn, in his book, gives two illustrations of the necessity for testing materials at temperatures other than room temperatures. In calculating the thickness of the wall of copper tubes for carrying superheated steam, the strength of cold wrought copper at normal temperatures must never be used in the calcu-

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[1] For considerations governing the experimental determination of mechanical properties at elevated temperatures, see RUDELOFF, *Proc.* 5th Cong. Int. Assoc. Test. Mat., Copenhagen, 1909, VI–1.

[2] *Comptes Rendus*, 1889, Vol. 109, p. 24. A noteworthy drop in the tensile strength of nickel was found between 300°C. and 350°C.

lation, because, if pure, the copper is completely annealed at temperatures below those readily attained in this instance. Furthermore, it would be wrong to use the strength of annealed copper at room temperature because the strength of copper changes with the temperature. It is necessary to test the copper at the temperature at which it will be used, *i.e.*, the temperature of the superheated steam. It is also commonly known that railway car axles break more readily in winter time than in the summer time. This is due, not so much to a change in the static tensile properties at the low temperatures, as it is to the very decided decrease in toughness, which is clearly brought out by the impact test on notched bars. Such cases should be sufficient to illustrate the desirability of extending the tests of our industrial metals and alloys to temperatures other than the ordinary testing temperatures.

A knowledge of the behavior of metals at elevated temperatures, would also be of undoubted technical importance in connection with the cutting and working of metals.[1] As yet there has been little or no work done and published, of this character, on which the rational mechanical treatment of metals at elevated temperatures can be based.

There are several noteworthy exceptions to the rule that the mechanical properties undergo great changes with change in temperature, the most conspicuous of which are undoubtedly the alloys of cobalt with chromium, molybdenum and tungsten which have as high tensile strengths when red hot as ordinary steels have at room temperatures.

The effect of raising the temperature on the properties of metals cannot, as yet, be stated in terms of any definite law; at present it is necessary to treat each class of materials separately. However, the behavior may be fairly generally stated by saying that the tensile strength and elastic limit decrease while the elongation and reduction of area increase with rise in temperature.

The most important class of materials to be considered here, the steels, furnishes a noteworthy exception to this rule. Rudeloff[2] and others[3] have shown that the tensile strength of steel

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[1] See, for example, the papers of Puppe, "The Power Required to Drive Rolling Mills," and "Investigations of the Pressures on the Rolls of a Cogging-Mill," Carnegie Sch. *Mem.*, 1910, Vol. 2, p. 271.

[2] Intern. Soc. Test. Mat., 1909, VI. The author discusses the principal points in connection with the testing of materials at elevated temperatures.

[3] See, for example, "Tests of Metals" from the Watertown Arsnal, 1888.

increases up to about 200°–300°C. where it reaches a maximum. The elongation drops rapidly from about 30 per cent. at room temperature to about 15 per cent. at the minimum which lies at about 150°–200°C. The yield point drops continually, slowly at first and then rather rapidly from 100° to 200°C. On the basis of the tensile strength alone, a structural steel would appear to improve with rise in temperature. This is misleading, as the increased strength is not available on account of the decrease in elongation and yield point, so that undoubtedly the best combination of properties is that secured over the ordinary ranges in temperature. The marked drop in elastic limit and elongation at 200°C., not as yet satisfactorily explained, produces what is known in steel as "blue brittleness," or excessive brittleness at the temperature corresponding to blue temper colors. On this account it is customary to carry on technological tests on the properties of mild steel at this temperature. These tests are of particular importance in the case of boiler plates, since the plates are not only used at these temperatures but they are weakened by being perforated with rivet holes. Deformations of considerable magnitude can be set up by non-uniform temperature variations which, under the above conditions, can lead to the failure of the boiler.[1]

The tensile strength and elastic limit of steel and other alloys increase below room temperature, while the elongation and contraction of area decrease; but the greatest change is in the toughness as measured on both plain and notched bars. The change in both ductility and toughness accounts for the numerous breakages of metals which are exposed to low winter temperatures which will be considered more in detail under the metallography of steel.

The variation in the physical properties of metals as the temperature is raised, depends, furthermore, on the previous history. This point is discussed by Rudeloff[2] who pointed out the difference between the behavior of annealed and hard drawn copper in this respect. The elongation of annealed copper remains fairly constant at 45 per cent. up to 300° whereupon it drops to 15 per cent. at 400°, while that of hard drawn copper runs fairly constant at about 8 per cent. up to 400° whereupon

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[1] A number of such failures were described in the "*Z*. f. Dampfkesselüberwachung," 1905, p. 319.

[2] *Loc. cit.*

it rises to 15 per cent.   Again the yield point of annealed copper decreased from about 500 kgs. to about 300 kgs. at 400°C. while the yield point for hard drawn copper dropped from 3200 kgs. to 300 kgs. at 400°C.   The exceptionally great drop in the yield point of hard drawn copper is due to the double effect of the raised temperature *per se*, and the secondary annealing effect of the elevated temperature on the hard drawn copper.

This double effect is again made apparent by the softening of hard drawn copper when tested at slow rates at high temperatures.   Thus, the values of the tensile strength and elastic limit are much less for the low rates of applying the load.   Le-Chatelier[1] found variations in the tensile strength of hard drawn copper at 250°C. from 34 kgs. to 18 kgs. as the duration of loading varied from 20 seconds to 30 minutes.

Hardness.—The property of hardness is another one which is difficult to define and equally difficult to measure.   Our simplest conception of a hard substance is one which cannot be readily scratched.   This is the use of the term as accepted by mineralogists and is the basis of the well-known scale of Mohs. However applicable this test may be in mineralogical determinations, it is not capable of rendering quantitative results which would be serviceable in the physical testing of materials.   For our purposes we may take hardness as the resistance of a material to abrasion or to cutting by a hard substance, or to penetration by another (harder) substance.   In some form or another, this is the property (or better, combination of properties, for we have no conception of hardness which permits us to classify it as a single property) which is measured by the methods commonly employed.   The different kinds of hardness are brought out by the different methods which are used to test for hardness, and, as a corollary, it is necessary to select the method with due regard for the particular kind of hardness which is to be measured.[2]

The Methods of Determining Hardness.—The most important method of measuring hardness in the engineering sense, and the one giving the most reliable results in the majority of cases, is

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[1] "Baumaterialienkunde," 1901, p. 157.

[2] As a matter of fact "hardness" which means resistance to cutting is in reality a combination of hardness with some other property, such as toughness.   Other kinds of "hardness" may be regarded as similar combinations. The term "hardness" is often incorrectly used to signify strength or even brittleness.   Inasmuch as this usage is not justified by the definitions of the terms and can only lead to confusion, it should be discarded.

the Brinell Ball Hardness Test. In the original or "Alpha" machine, a hydraulic ram forces a steel ball (10 mm. in diameter) under a pressure of 3000 kg. into the prepared surface of the test specimen. The steel ball used is an ordinary hardened ball bearing, one that will not deform materially during the test. In one of the simpler forms of this apparatus, the pressure is applied by means of a small oil pump and is measured by means of a gage. The piston is attached to a cross arm which is weighted at either end with a certain load, so gaged that as soon as the pressure reaches the desired amount, the cross arm is raised. This pressure is applied for a definite length of time, usually one-half minute, and is then released.

The hardness of the material is expressed as a hardness number, H, which is obtained by dividing the load applied in kilograms, K, by the superficial area of the concavity left in the surface of the material, y, in square millimeters. Thus $H = \dfrac{K}{y}$, where

$$y = 2\pi r\left(r + \sqrt{r^2 - \frac{D^2}{4}}\right)$$

in which r is the radius of the ball and D the diameter of the depression. Tables are supplied with the testing machine from which the hardness number, H, can be obtained from the diameter of the depression measured in millimeters. A special microscope is supplied with the apparatus for measuring the diameters. Hardness numbers are given for pressures of 500 kg. (for soft metals) and 3000 kg.[1]

Martens devised an apparatus for carrying out the Brinell test which merits description.[2] The pressure is supplied from below by means of a diaphragm which gives a very uniform distribution of the pressure and eliminates the piston friction in the Alpha machine. In this manner the specimen is forced up against the steel ball. The hardness number is secured from the pressure and the depth of penetration (measured to 0.001 mm.), as measured by the displacement of a mercury column, which gives a very sensitive and accurate determination. The depth

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[1] A detailed discussion of the Brinell test and of the conditions which must be fulfilled to secure an accuracy of ± 5 in the hardness number has been given by GRARD, *Proc.* 6th Cong. Int. Soc. Test. Mat., New York, 1912, III, 2.

[2] MARTENS and HEYN, *Zeit.* Ver. deut. Ing., 1908, Vol. 52, p. 1719; also, *Proc.* 5th Cong. Intern. Soc. Test. Mat., Copenhagen, 1909.

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of penetration is used, in preference to the diameter of the depression, as its variation with the hardness is more nearly linear.

Ludwig[1] suggested combining the Brinell test with the Kerpely test, and substituted a conical point (angle of the point = 90°) for the customary hardened ball. The load on the point is measured in kilograms, G, and the depth of penetration is measured in millimeters, t. The hardness number is equal to

$$\frac{P}{4.44t^2}$$

Another method for measuring hardness is the one devised by Shore,[2] which is based upon the assumption that the height to which a small, diamond-pointed steel pellet rebounds from the prepared surface of the test specimen, is proportinal to the hardness, the height of fall being kept constant. The height of rebound is then proportional to the resistance to penetration by impact, which is offered by the material.

In order to secure reliable results, it is necessary to impose the condition that the hammer must produce a permanent deformation; otherwise the surface elasticity and not the "hardness" would be the chief factor in determining the height of the rebound.

A third method which is commonly used to measure hardness is the sclerometric method by which the resistance to scratching by a fine point or to cutting by a drill, is determined. The simplest application of this method is the determination of mineralogical hardness according to the Mohs scale, already referred to.[3]

The sclerometer which is now most commonly used is one devised by Turner[4] and modified by Martens[5] and has proven to be most useful in the scientific investigation of metals and alloys.

[1] See LUDWIG, "On the Determination of Hardness," Baumaterialien-kunde, 1907, Vols. 8, 9, 10; In this test Kick's law of proportional resistances is utilized and the hardness number is independent of the load, P. See also MEYER, "On Hardness and Its Determination," *Zeit.* Ver. deut. Ing., 1908, pp. 645, 2077.

[2] *The American Machinist*, 1907, Vol. 30, Pt. 2, p. 747. See also MEYER, *Phys. Zeit.*, 1908, Vol. 9, p. 66; and R. DE FRÉMINVILLE, *Rev. de Met.*, 1908, Vol. 5, p. 329; SPRINGER, *Iron Age*, 1908, Vol. 82, p. 555; SHORE, *Trans.* Am. Soc. Test. Mat., 1910.

[3] A scale of hardness using 18 different metals was suggested by Göllner, as used at Prague, *Proc.* Inst. Civil Eng., 1882, Vol. 73, Pt. 3, p. 456.

[4] *Proc.* Birmingham Phil. Soc., 1886, Vol. 5, p. 291.

[5] A. MARTENS, *Mitt. k. techn. Versuchs-Anst.*, 1890, Vol. 8, p. 236.

The test is accomplished by scratching the polished surface of the test specimen with a standard diamond point, under a standard pressure, usually 20 grams. The specimen is embedded in plasticene on a movable stage with the polished surface upward so that, by turning a small thumb screw, the specimen is moved horizontally underneath the diamond point. The width of the scratch produced is thereupon measured under a microscope and the hardness is given by $H = \dfrac{1}{a}$, where a is the width of the scratch in millimeters. The hardness is sometimes taken as the load in grams necessary to produce a scratch 0.01 mm. in width. The difference in hardness between two microconstituents is readily determined by this method. The surface is first polished, then scratched and later lightly etched so as to bring out the different constituents. The constituent which shows the narrower scratch is the harder of the two. In this manner the relative hardness of ferrite and cementite and of martensite and austenite in steel can be determined.

A "Micro-sclerometer" has been devised by Jaggar[1] for the purpose of determining the hardness of the microconstituents of rocks and minerals. In the same form, it has been used by Boynton[2] to determine the hardness of the various constituents of iron and steel. A small diamond point is loaded with a weight of 10 grams and used as a drill to penetrate the surface of the material. It is rotated by clock work at a constant speed and the number of rotations necessary to cause a penetration of 0.01 mm. is taken as the hardness number. The entire operation is done on the stage of the microscope.

The method of determining the "abrasion hardness" or resistance to wear, as well as the results of tests of carbon and alloy steels, have been given by Robin[3]. This method, which undoubtedly gives comparable results and is capable of yielding mportant information, has not been extensively employed.

The three principal methods for testing hardness appear to have separate fields of usefulness. For scientific work, the Martens sclerometer undoubtedly gives the most accurate results, while the ball hardness test is equally as useful in the testing of materials, as its results are most concordant with

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[1] *American Journal of Science*, 1897, Vol. 4, p. 399.

[2] *Journ.* Iron & Steel Inst., 1906, No. 2, p. 287; 1908, No. 2, p. 133.

[3] Carnegie Sch. *Mem.*, 1910, No. 2, p. 1.

engineering practice. The scleroscope occupies a peculiar position in that while its results are entirely empirical and do not measure any kind of hardness as just discussed, it is particularly adapted to certain routine determinations in works practice and in measuring small differences in relative hardness. Regarding the empirical nature of the determinations of the scleroscope, we may quote Heyn as follows.[1]

"Inasmuch as the scale divisions of the Shore hardness tester and the point 100 are arbitrary and therefore cannot be subsequently checked at any time, the apparatus can not be calibrated. Agreement among the results obtained with different instruments depends solely upon the care exercised by the maker. No possibility exists for the purchaser to find out whether his results check those of other instruments of the same make. The standard, which is supplied, does not alter this because it cannot be determined to what extent the test bar checks at different places as to the nature of the material and the hardening.

"Such a condition may well be conceivable from the standpoint of the maker of the instrument, but it runs counter to the most important principle of the testing of materials. This requires that all apparatus must have accession to (be calibrated in terms of) recognized systems of measurement (feet, pounds, etc.) and that the calibration can be subsequently checked at any time independent of the maker."

However severe the above criticism may be, it is levelled mainly at the use of the apparatus as a scientific instrument and does not bring out anything to militate seriously against the use of the scleroscope in its natural and well-defined fields. Far greater difficulties are encountered, in practice, due to the conditions of the test, among which may be mentioned the following: Very appreciable errors may be introduced (1) in anvil testing, by the faces of the test specimen not being parallel and by lack of tight contact with the surface; (2) in vise testing, by failure to clamp the specimen tightly and to have the surface perfectly level. In all cases the condition of the surface, decarburization and superficial blow holes, can also affect the results.

Continuing, Heyn points out that the modulus of elasticity, the yield point, the resistance of the material to permanent deformation, etc. (all of which are included in th scleroscope "hardness"), all affect the results, and to such an extent that different materials with different elastic properties can give rebounds which are not commensurate with their real hardness.

[1] "Materialienkunde," II A, p. 410.

The empirical nature of the method and of the principle on which it is based is made clear by the following table, which compares Brinell hardness numbers, taken from the work of Brinell, and scleroscope hardness numbers, as taken from the data of Shore,[1] reduced to a common scale.

TABLE 15.—COMPARISON OF BRINELL HARDNESS AND SCLEROSCOPE HARDNESS

Metal	Brinell number for lead = unity	Scleroscope number for lead = unity
Lead	1.0	1.0
Tin	2.5	3.0
Babbitt metal	4.0	1.3–3.0
Zinc	8.0	3.0
Gold	8.4	1.7
Silver	10.3	2.1
Brass	11.0	2.5–12.0
Mild steel (0.15 per cent. C)	17.5	8.0
Tool steel (1 per cent. C)	45.5	10.0
Same hardened	111.0	33.0

The above table, by the vast difference between the corrected scleroscope number and the corrected Brinell number, brings out the deficiency of the elastic rebound method to measure "hardness." In fact the small difference in hardness between mild steel and tool steel, according to the shore scleroscope, is very surprising.

Another weakness of the scleroscope is that of measuring relative hardness over a cross section. Thus the author has results of hardness determinations over the cross section of a heat treated bar, $\frac{3}{4}$ inch in diameter, as measured by the Brinell test and by the scleroscope. Whereas the ball hardness number averaged 197 around the rim, and the scleroscope 15.5, the Brinell number for the interior was 163, while the scleroscope number was 29.[2] Devries, in a publication of the Bureau of

[1] "The Shore Scleroscope," Seventh Edition.

[2] The dependence of the scleroscope number on the thickness of the specimen and the distance in from the edge of the specimen, is undoubtedly very complex and has been considered in some detail by HOWE and LEVY, *Proc. Amer. Soc. Test. Mat.*, 1916, Pt. II, p. 36. The increase in scleroscope number referred to is probably due to the greater resiliency at the middle of the test piece.

Standards,[1] pointed out that the static tests gave rational results but that the dynamic tests (Shore and Ballantine) did not agree in general with the static tests. These conclusions are supported by the work of Roush[2] who points out further that the scleroscope number is not even proportional to the elastic limit, as is claimed by the maker.[3]

In the light of all these deficiencies in the Shore test, both theoretical and experimental, it is evident that the scleroscope hardness numbers cannot be relied upon to give positive determinations of the hardness, and, under certain circumstances, not even of the relative hardness.[4] The fact remains, however, that a particular material, when treated in a certain manner and tested in a certain prescribed manner will show a certain scleroscope "hardness." Any variation in the treatment, assuming the manner of testing to remain the same, will result in a different determination. On this account the scleroscope is very useful as a ready means of controlling many technical operations such as case hardening machine parts, annealing, cold rolling, etc., especially if the same operation is repeated a large number of times and the same end point is desired in each case. This applies particularly if the modulus of elasticity remains constant throughout the operations. A decided advantage in favor of the scleroscope test is that determinations can be made on finished pieces without injury to them. Thus the scleroscope, while of little value in scientific research work, supplies a very handy, and in many cases sufficient control of

[1] *Technologic Paper* No. 11. "Comparison of Five Methods used to Measure Hardness." The tests were the Brinell, Ludwik, Shore, Ballentine and the Bauer drill test.

[2] "Hardness and Its Measurement," *Met. & Chem. Eng.*, 1910, Vol. 8, p. 578.

[3] On the other hand, we have evidence that if the scleroscope is calibrated, so to say, against tensile strength for a particular series of steels in which the modulus of elasticity remains constant, the readings may be taken as a measure of the strength. Thus ABBOTT (*Proc. Amer. Soc. Test. Mat.*, 1915, Vol. 15, II, p. 42) has shown that there is an approximate proportionality between scleroscope numbers and tensile strength of various grades of carbon, nickel, chrome-nickel, and chrome-vanadium steels, heat treated in different manners. It is particularly valuable to know these relationships when the tensile strength runs above 200,000 lb.

[4] According to Mather, cast iron castings which machine very easily have a scleroscope number of 30, while hard castings have a scleroscope number of only 36 or 37. *Foundry*, 1909, Vol. 36, p. 34.

technical operations which have been previously worked out and standardized.[1]

The Hardness of Metals and Alloys.—While the hardness of the elements has not been carefully determined as yet, at least with sufficient accuracy to establish a definite law, still it has long been recognized that hardness and atomic volume are very closely related; *i.e.*, as the atomic volume increases the hardness decreases. This is illustrated by the following table which gives the atomic volume and hardness of different elements.[2] Just recently it was pointed out by Edwards that

TABLE 16—HARDNESS OF THE ELEMENTS

Element	Atomic volume	Hardness number	(A)
Nickel	6.7	1410	144
Manganese	6.9	1456	210 (?)
Cobalt	6.9	1450	86
Iron	7.2	1375	97
Copper	7.2	1360	53
Palladium	...	1200	61
Chromium	7.7	....	91
Platinum	9.1	1107	44.3
Zinc	9.1	1077	45.5
Silver	10.2	990	37
Iridium	....	984	217
Gold	10.2	979	33
Aluminum	10.6	821	24.7
Cadmium	12.9	760	29
Magnesium	13.8	726	38.3
Tin	16.1	651	15.6
Lead	18.1	570	6.95
Thallium	....	565	7.3
Bismuth	21.1	...	14
Calcium	....	405	22.2
Sodium	23.7	400	0.07
Potassium	45.4	230	0.037

(A) EDWARDS, *Journ.* Inst. of Metals, 1918, No. 2, p. 61.

[1] MATHEWSON and PHILLIPS remark, in their work on annealing cold rolled α brass, that with the scleroscope, accurate determinations of the "softening" temperature can be made. This, and other examples, could be cited to illustrate the usefulness of the test.

[2] TURNER, *Journ.* Iron & Steel Inst., 1909, No. 1, p. 426.

hardness is not a direct but a periodic function of the atomic volume, and that there is an even greater similarity between the periodicities of hardness and the absolute melting points. Edwards' figures are included in table 16.

The hardness of binary alloys varies with the constitution according to laws similar to those governing the variation of electrical resistance.[1] These laws can be expressed as follows:

The hardness of heterogeneous mixtures of two phases, whether they be pure metals, saturated solid solutions or intermetallic compounds, varies approximately as a linear function of the composition. Eutectics, eutectoids and fine grained aggregates are somewhat harder than would be calculated from their composition.

The hardness of isomorphous solid solutions varies similarly to the electrical resistance, as is illustrated by the gold-silver alloys. The (sclerometric) hardness increases to a maximum at about equal atomic percentages of gold and silver, at which point the hardness is approximately twice as great as of either constituent. In the same way the hardness of dilute solid solutions of iron with manganese, silicon, phosphorus and carbon, increases in proportion to the atomic per cent. of the dissolved metal.[2]

The hardness of intermetallic compounds is generally greater than that of either component. Otherwise the variation in hardness is as given above. If the compound does not form solid solutions with the adjacent phases, the hardness curves consist of two straight lines intersecting at the compound. If the compound forms solid solutions with the adjacent phases, the compound is characterized by a cusp pointed downwards. This case is illustrated by the alloys of magnesium and cadmium.[3]

Commercial Applications.—The hardness of materials of engineering is determined as an indication of their strength, ductility, wearing properties, resistance to penetration, etc. It

[1] KURNAKOFF and SCHEMTSCHUSCHNY, *Zeit.* anorg. Chemie, 1908, Vol. 60, p. 1.

[2] BENEDICKS, "Recherches physico-chèmique des aciers au carbonne," Upsala. Campbell states that equal molecular concentrations of carbides in solution exert equal influences on the specific resistance. *Trans.* Faraday Soc., 1917, Vol. 12, p. 274

[3] See URAZOW, *Zeit.* anorg. Chemie, 1911, Vol. 73, p. 31.

is, therefore, of interest to note the special applications of the different methods now used and to compare the results with one another. As was stated above, the Brinell ball hardness test gives results which are most comparab e to service conditions. This applies to the hardness of steels, both as affected by chemical composition and heat and mechan'cal treatments, as an indication of the wearing qualities and engineering value. The Shore scleroscope serves chiefly as an indication of the heat treatment of any one steel, *i.e.*, case hardening etc., and to detect irregularities, but not necessarily to show the nature of those irregularities.

There has been an attempt made to correlate the hardness of the material and its tensile properties. Such a comparison cannot be looked upon as being scientifically accurate but, that it gives valuable information in connection with certain known materials, there is no doubt.[1] The figures in Table 17, from the data of Abbott, are given to show the variation in Brinell and scleroscope hardness for two values of the tensile strength, and in tensile strength and scleroscope hardness for two values of the Brinell hardness, and in tensile strength and Brinell hardness for two values of the scleroscope hardness. The per cent. varia-

TABLE 17.—VARIATION IN BRINELL AND SCLEROSCOPE HARDNESS FOR A GIVEN TENSILE STRENGTH

Material	T. S., lbs. per sq. in.	Brinell		Scleroscope	
		Range	Per cent.	Range	Per cent.
Carbon steel..................	80,000	130–170	26	19–29	42
	240,000	340–405	17	56–70	22
3.5 per cent. nickel steel......	80,000	133–170	24	17–27	45
	240,000	345–440	24	56–81	36
Chrome-vanadium steel........	80,000	130–170	26	18–29	47
	240,000	348–453	26	55–77	33
0.5 per cent. Cr–1.5 per cent. Ni steel	80,000	122–180	38	17–28	49
	240,000	328–470	35	56–77	31
1.0 per cent. Cr—3.5 per cent. Ni steel..................	80,000	133–170	24	18–25	32
	240,000	338–435	25	55–84	42

[1] See McWilliam and Barnes, "Brinell Hardness and Tenacity Factors of a Series of Heat Treated Special Steels," *Journ.* Iron & Steel Inst., 1915, No. 1, p. 125.

VARIATION IN TENSILE STRENGTH AND SCLEROSCOPE HARDNESS FOR A GIVEN BRINELL HARDNESS

Material	Brinell number	Scleroscope		Tensile strength	
		Range	Per cent.	Lbs. per sq. in.	Per cent.
Carbon steel.............	120	15–27	57	55,000– 70,000	24
	360	53–70	27	210,000–250,000	17
3.5 per cent. nickel steel...	120	14–22	44	50,000– 68,000	30
	360	48–75	46	188,000–250,000	28
Chrome-vanadium steel...	120	14–24	53	52,000– 70,000	30
	360	48–76	45	190,000–250,000	27
0.5 per cent. Cr—1.5 per cent. Ni steel..........	120	12–22	44	45,000– 78,000	54
	360	50–75	40	178,000–268,000	40
1.0 per cent. Cr—3.5 per cent. Ni steel..........	120	13–19	37.5	50,000– 68,000	30
	360	49–77	44.0	193,000–258,000	29

VARIATION IN TENSILE STRENGTH AND BRINELL HARDNESS FOR A GIVEN SCLEROSCOPE HARDNESS

Material	Sclero-scope number	Brinell		Tensile strength	
		Range	Per cent.	Lbs. per sq. in.	Per cent.
Carbon steel............	20	73–155	72	33,000– 83,000	86
	60	305–405	28	200,000–258,000	25
3.5 per cent. nickel steel..	20	112–168	40	57,000– 90,000	45
	60	290–440	41	177,000–253,000	35
Chrome-vanadium steel..	20	100–162	47	50,000– 90,000	57
	60	290–446	42	180,000–265,000	38
0.5 per cent. Cr—1.5 per cent. Ni steel........	20	110–160	37	50,000– 92,000	39
	60	292–422	36	184,000–250,000	30
1.0 per cent. Cr—3.5 per cent. Ni steel........	20	122–164	29	68,000– 86,000	23
	60	290–430	39	174,000–250,000	36

COMPARISON OF AVERAGE BRINELL AND SCLEROSCOPE HARDNESS NUMBERS FOR A GIVEN TENSILE STRENGTH FOR DIFFERENT MATERIALS

T. S., lbs. per sq. in.	Carbon		3.5 per cent. Ni		Cr–V		0.5 per cent. Cr–1.5 per cent. Ni		1.0 per cent. Cr–3.5 per cent. Ni	
	Scl.	Br.	Scl.	Br.	Scl.	Br.	Scl.	Br.	Scl.	Br.
80,000	24	148	22	158	24	152	22	148	23	158
240,000	61	368	69	384	62	378	65	384	65	384

COMPARISON OF BRINELL HARDNESS NUMBERS WITH AVERAGE SCLERO-
SCOPE HARDNESS NUMBERS FOR DIFFERENT MATERIALS

Brinell No.	Carbon, scl.	3.5 per cent. Ni, scl.	Cr–V, scl.	0.5 per cent. Cr–1.5 per cent. Ni, scl.	1.0 per cent. Cr–3.5 per cent. Ni, scl.
120	19	14	17	16	13
360	62	62	61	61	63

tion is calculated from the actual variation divided by the mean value. [1]

These figures are offered for what they may be worth but they show how cautious we must be in computing the tensile strength from hardness determinations.

The Brinell and Shore tests can be combined as a test in case-hardening practice. The Brinell ball hardness test gives values which depend, not only on the superficial hardness, but on the depth of carburization. The results obtained by the Shore scleroscope indicate the surface hardness and are independent of the depth of carburization, provided the amount of superficial carbon exceeds 0.8 per cent.[2] By combining these two tests, case hardened steel can be tested for superficial hardness, depth of carburization, and efficiency of the heat treatment. ·

[1] WAHLBERG, *Journ.* Iron & Steel Inst., 1901, No. 1, p. 243; No. 2, p. 234; and H. Le CHATELIER, *Rev. de Mét.*, 1906, Vol. 3, p. 689, have established numerous relationships which are of technical interest. GRARD, "Research on the Hardness of Steel," *loc. cit.*, gives the relation between hardness and tensile strength for different steels under different heat treatments as well as the precautions which are necessary to insure accuracy in the hardness number. The resistance of steel to abrasion and the effect of impurities are discussed by ROBIN, *Rev. de Mét.*, 1911, Vol. 8; *Comptes. Rendus*, 1910, Vol. 151, p. 710.

[2] See PORTEVIN and BERJOT, *Rev. de Mét.*, 1910, Vol. 7, p. 61.

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